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THE

PHYSICAL REVIEW.

PHYSICAL PROPERTIES OF THIN METALLIC FILMS.[1]

III. The Effect of Temperature on the Change of Resistance of Bismuth Films in a Magnetic Field.

By L. F. Curtiss.

Synopsis.

Ageing of sputtered bismuth films.—The films sputtered on glass between sputtered gold terminals, were sealed in glass tubes and kept in vacuo at 210–220° C. for a number of hours. As a result each film showed a gradual *decrease of resistance* amounting in all to about 40 per cent. Eventually the films became so thoroughly aged that temperature-resistance measurements in vacuo could be accurately reproduced over long periods.

Increase of resistance of bismuth films in a magnetic field for temperatures from − 190° to 230° C.—The isothermal curves obtained for each film by varying the field up to 18,000 gauss, have the same form for all temperatures, differing only by constant factors, and closely resemble the corresponding curves for bismuth in bulk. The percentage increase of resistance is not proportional to the square of the field. It is greater the lower the temperature and the lower the resistance, that is, the thicker the film, reaching a value about 1/5 that of bismuth for the thickest film tested.

Variation of resistance of bismuth films with temperature, − 190° to 230° C.—The curves are parabolic in form, showing a minimum around 150–200° C.; the lower the resistance of the film, the lower the temperature of minimum resistance.

Electrically heated oil bath.—It is suggested that bakelite is a suitable material for protecting the nichrome heater.

THIS work continues the investigation of the behavior of the resistance of bismuth films in a magnetic field described in the second[2] paper of this series. A study of the change of resistance of these films in a magnetic field at various constant temperatures from near the melting point of bismuth down to liquid air temperatures has here been undertaken.

[1] Third of a series of articles on this subject from the Physical Laboratory of Cornell University. This series of articles was made possible by a grant to Prof. F. K. Richtmyer from the Rumford Fund.

[2] F. K. Richtmyer and L. F. Curtiss, Phys. Rev., 15, p. 465, 1920.

For this purpose thoroughly aged films were desirable, since only with films which have been subjected to a thorough heat treatment can reproducible results be expected, as is evident from the results of the previous work referred to above. Since the oil bath had not been entirely satisfactory because of its destructive action on the films, it was thought advisable to try some other means of protecting the films from the action of the air during the heating. The procedure which suggested itself was to place the films in flat glass tubes and to evacuate the tubes to as high a degree as possible with a Langmuir mercury vapor pump, at the same time heating them and the enclosed films to near the melting point of bismuth. This heating served two purposes. It gave the films a preliminary heat treatment and it also helped to free the film and tube from adsorbed gases, thus affording a greater protection to the film during subsequent heatings.

The films were prepared in much the same way as for the previous work (*loc. cit.*). The glass slides on which the metal was deposited were made somewhat narrower for convenience in inserting them into the flat glass tubes. The actual dimensions of the bismuth film itself, however, were kept the same as those used formerly, *i.e.*, 10 by 3 mm. The rotating sector was dispensed with and a kenotron[1] for rectifying the secondary current of the transformer was placed in series with the discharge jar. This improvement cut out the reverse current and eliminated its heating effect, thus rendering the rotating sector unnecessary for the preparation of films for the present purpose. It also made possible the sputtering of much thicker films than had previously been possible. For, as stated in the preceding paper, after sputtering a certain length of time the surface of the bismuth film becomes gray and powdery and further sputtering has little effect upon the resistance of the film, since the particles of metal which come down seem no longer to adhere to the metal already deposited firmly enough to become active in conducting the current. It was found that this condition did not come about as soon when the kenotron was used.

The successive steps in the manufacture of a film are illustrated in the diagrams in Fig. 1, which are drawn to scale. First the glass slide was thoroughly cleaned chemically, rinsed with distilled water and dried. It was then covered across the middle squarely with a glass slide exactly 1 cm. wide with edges ground true and gold terminals were deposited on the exposed ends by cathodic sputtering, after which it had the appearance indicated in Fig. 1, *a*. Then a shield of mica with a slot 3 mm. wide and long enough to overlap the gold terminals was placed on this blank and a bismuth film deposited, likewise by cathodic sputtering,

along the center of the slide connecting the two gold terminals, as shown in Fig. 1, *b*. A piece of fine bare copper wire was then wrapped tightly around each end as shown in Fig. 1, *c*. A thin layer of hot paraffin was spread across the face of the film, near the ends of the bismuth, which prevented the copper sulphate solution, used in plating the wires in position, from creeping up on to the bismuth. This was later dissolved off with xylol. First one end, then the other, of the film was dipped into the plating bath and a thick coating of copper deposited on the gold film and copper wire, the projecting wires serving as leads for the current in each case so that it did not pass through the bismuth film. This plated terminal insured positive contact with the film at all temperatures and proved to be far superior to the clamps which had been used before for this purpose. The film at this stage had the appearance shown in Fig. 1, *d*. Short pieces of Cunife wire were then welded onto the projecting ends of the copper wires for sealing through the glass and then longer pieces of copper wire were welded onto the Cunife to serve as external leads after the films had been sealed into the glass tubes. The tubes were prepared from flat glass tubing by sealing a short piece of glass tubing at right angles near one end for attaching to the pumps. The film with its lead wires was then sealed in and the tube sealed on to the pumps and evacuated for several hours at about 210° C. with a Langmuir pump, after which it was sealed off. The general arrangement of the film within its evacuated tube is also shown in Fig. 1. The

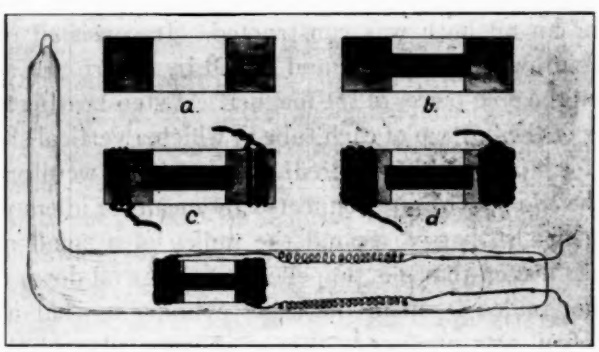

Fig. 1.

film was now further aged by heating for four hour periods to about 220° in an oil bath. These heatings were repeated four or five times for each film after which it had become relatively stable and further heating had very little effect upon its resistance at room temperature.

[1] Kindly loaned by Prof. J. S. Shearer.

It is interesting to note that all films, without exception, *decreased* in resistance as a result of this heating. This is quite contrary to the effect produced by heating bismuth films in air, or even in an oil bath, since only in the case of two films out of a couple of dozen did such an effect occur in the previous work (*loc. cit.*). Thus Film V–5 had a resistance of 36.7 ohms at room temperature after it had been sealed into a glass tube and the tube exhausted. After it had been subsequently heated for four hours at about 220° its resistance at room temperature was only 21.7 ohms, thus decreasing about 41 per cent. in resistance during this treatment. Similarly Film V–13 had a resistance after being sealed into a tube of 30.8 ohms and after heating eight hours to about the same temperature it had a resistance of 17.8 ohms, or had decreased about 42 per cent. in resistance. Other films showed comparatively smaller changes during this aging process and in consequence were less stable, and showed further decreases in resistance during subsequent measurements at the higher temperatures. Thus the resistance of Film V–9 was 10.9 ohms after having been sealed into a tube and after heating for four hours its resistance was 7.4 ohms, decreasing about 33 per cent.; similarly Film V–14 had a resistance of 100.0 ohms after it was sealed into a glass tube and after heating eight hours its resistance was 83.6 ohms, decreasing only sixteen per cent. Before the final measurements on this film had been taken, however, it had decreased to about 55 ohms.

For measurements in the field at room temperature and above, a brass container for an oil bath was constructed. It consisted of two brass tubes, each cut away on one side and joined by a narrower neck so as to fit in between the pole-pieces of the magnet. A step-bearing was fastened in the center of the bottom of each tube in which a vertical shaft carrying a propeller for stirring was mounted. These shafts were provided with pulleys at the top which were connected by means of idlers with an endless belt which also passed around the pulley of a small motor. The shafts were so driven that one propeller forced the oil down one cylinder and the other pulled it up in the other cylinder so that a continuous circulation of oil was produced. Fig. 2 shows a plan of the container and illustrates its position with reference to the pole-pieces of the magnet. The bath was about 12 cm. deep and 22 cm. from the outside of one cylinder to the outside of the opposite cylinder. The distance between the pole-pieces was one centimeter. The bath was heated by a resistance element made by winding nichrome ribbon on a sheet of mica. It was found that some protection for the ribbon was necessary since the oil, although it was a good grade of gas-engine cylinder oil, carbonized badly

at the higher temperatures and adhered to the ribbon, thus short-circuiting adjoining turns. Bakelite was found very satisfactory for this purpose. The current through the heating element could be controlled by rheostats so that the temperature could be brought to any desired value and held constant for considerable intervals of time. The temperatures were measured with a copper-advance thermo-couple made and calibrated in the usual way. Its e.m.f. was measured by a Leeds and Northrup potentiometer.

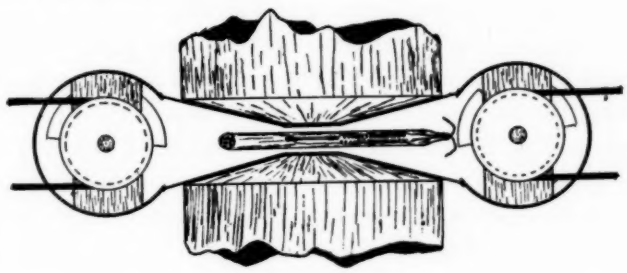

Fig. 2.

Since simultaneous measurements of field strength and resistance of the film were impracticable, a calibration of the magnet was made before the temperature bath was inserted between the pole-pieces. This was done by means of a bismuth spiral, calibrated for the purpose by the Bureau of Standards. Especial precautions were taken to keep the spiral during these measurements at the constant temperature at which it had been calibrated. By this means a curve between the current through the magnet coils and the strength of the resulting field in kilogauss was obtained which was used in determining the field throughout the experiments at room temperature and above. Control experiments showed that this method would give results which could be depended upon to within less than one per cent., which was deemed adequate for the present work. The current for the magnet was supplied by a set of twenty-six 15-ampere storage cells connected in series. The maximum current used in this part of the work was about seven amperes. A large Weston Laboratory Standard millivoltmeter and shunt were used in measuring the magnet current both during the calibration and throughout the subsequent experiments.

For convenience, all the measuring instruments and controlling rheostats were mounted on a table so that they were all under the control of one operator. Thus all factors could be varied by a single person without shift of position during an experiment. This also made possible a simultaneous determination of the various quantities, eliminating

errors due to variation in the temperature or in the current through the magnet.

In making the measurements the procedure was as follows: The film was placed in its position in the oil bath and the rheostats controlling the current through the heating element were adjusted. About twenty minutes were necessary for the temperature to become steady. As soon as the potentiometer readings indicated that this state had been reached, measurements of the resistance of the film were made at various values of the current through the magnet coils, checking the zero-field resistance of the film and the potentiometer reading after each measurement. It was found possible in all cases to hold the temperature steady enough so that the zero-field resistance of the film did not vary more than 0.1 per cent. during a series of measurements at a given temperature. The results of the measurements can best be presented by a discussion of the curves plotted from the data taken with typical films. A set of data for one of the films, V–5, is given below to illustrate the magnitude of the quantities involved.

FILM V–5.

Potentiometer Reading, 0.001010; *Temperature*, 23.5°; *Resistance of leads*, 0.370 *ohms*.

Magnet Current.	Bridge Reading.	Resistance of Film.	dr	dr/r	H (Gauss).
1.0	21.603	21.233			
0	21.509	21.139	0.094	0.0044	2300
2.0	21.862	21.492			
0	21.516	21.146	0.346	0.0164	4725
3.0	22.219	21.849			
0	21.502	21.132	0.717	0.0339	7250
4.0	22.682	22.312			
0	21.498	21.128	1.184	0.0561	9700
5.0	23.170	22.800			
0	21.492	21.122	1.678	0.0795	11950
6.0	23.660	23.290			
0	21.492	21.122	2.168	0.1028	14125
6.84	24.014	23.644			
0	21.493	21.123	2.521	0.1196	15710

Another set of data for the same film at 230°, the maximum temperature at which measurements were made on this film, is given below also.

Temperature variations are more likely to occur and the zero-field resistance of the film is not as constant as in the set taken at room temperature. However the variations in it are still less than 0.1 per cent.

Potentiometer Reading, 0.011241; *Temperature*, 229.3°.

Magnet Current.	Bridge Reading.	Resistance of Film.	dr	dr/r	H
0	20.957	20.587			
1.0	20.943	20.573			
0	20.930	20.560	0.013	0.0005	2300
2.0	20.965	20.595			
0	20.938	20.568	0.027	0.0013	4725
3.0	21.001	20.631			
0	20.930	20.560	0.071	0.0034	7250
4.0	21.039	20.669			
0	20.930	20.560	0.109	0.0053	9700
5.0	21.086	20.716			
0	20.925	20.555	0.161	0.0078	11950
6.0	21.141	20.771			
0	20.923	20.553	0.218	0.0106	14125
6.8	21.186	20.816			
0	20.921	20.551	0.265	0.0129	15650

For measurements at low temperatures the oil bath was removed from between the pole-pieces of the magnet, and, to make possible better heat insulation, the pole-pieces were separated to a distance of 1.8 cm. The exposed parts of the magnet in between the coils were covered with a thick layer of heat insulation, a thinner layer also covering the faces of the pole-pieces. A cardboard container for the refrigerant was lowered into the rectangular compartment thus formed. A vertical section is shown in Fig. 3 which will give an idea of the arrangement.

Since the pole-pieces of the magnet had been separated to a greater distance it was necessary to increase the current through the coils, beyond that which was used during the experiments at the higher temperatures, in order to cover the same range of field strengths. The magnet was accordingly connected to the 110-volt direct current supply of the laboratory through suitable rheostats. This arrangement was not as satisfactory as the storage battery had been since the fluctuations

in the line voltage caused small variations in the magnet current. However, by exercising extreme care, errors from this source could be reduced to a negligible amount. The maximum current used was about 18 amperes, giving a field of about 18,000 gauss. The magnet was recalibrated, a ballistic galvanometer, a standard of mutual inductance, and a snatch coil being used for this purpose, since an accident to the bismuth spiral had ruined it.

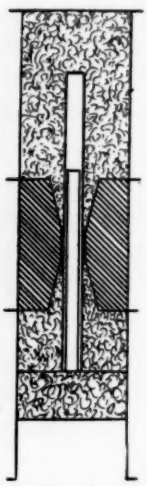

Fig. 3.

The films were removed from their protecting glass tubes for the measurements at low temperatures, as they have very slight tendency to oxidize at room temperature and below, and a considerable saving of space between the pole-pieces was thereby accomplished. They were mounted on a fiber support by means of which they were accurately centered between the pole-pieces. One junction of a thermo-couple for measuring temperatures was also mounted on the fiber strip so that it was close to the film.

Great difficulty, due to poor heat insulation and the conductivity of the large pole-pieces, was experienced in maintaining constant temperatures for any considerable period of time unless the films were actually immersed in the refrigerant. Consequently measurements in the field were only attempted when the films were immersed in either a mixture of carbon dioxide snow and ether or in liquid air.

The results of the investigation can be considered under four heads, viz., (1) effect of magnetic field on the resistance of the films at various temperatures; (2) the dependence of the values of the percentage increase of resistance upon the thickness of the film; (3) evidences of aging of the films; (4) relation between the temperature of the film and its resistance.

Observations were made on the behavior of a large number of films varying in resistance from 7 ohms to 70 ohms. No attempts were made to measure the thickness of the films. Since all of the films had the same length and breadth, the resistance can be taken as a rough indication of the thickness. Film V–10 has been selected as an example for a discussion of the effect of temperature upon the percentage increase of resistance of the films in a magnetic field. At 20.5° its resistance was 10.54 ohms, hence it was one of the thicker films studied. The results of the measurements on this film at various temperatures are shown graphically in Fig. 4. The percentage increase of resistance has been plotted against the field strength in kilogauss. The various curves have been labelled and were taken at the following temperatures:

I.....	20.5°	IV.....	147.5°	VII.....	− 80°
II.....	57.2°	V.....	195°	VIII.....	− 190°
III.....	109.0°	VI.....	227°	A.....	19.5°

As the temperature decreases the effect of the field becomes more strongly marked, especially at the low temperatures. For the weaker fields there is a decided curvature in the lines which gradually smooth

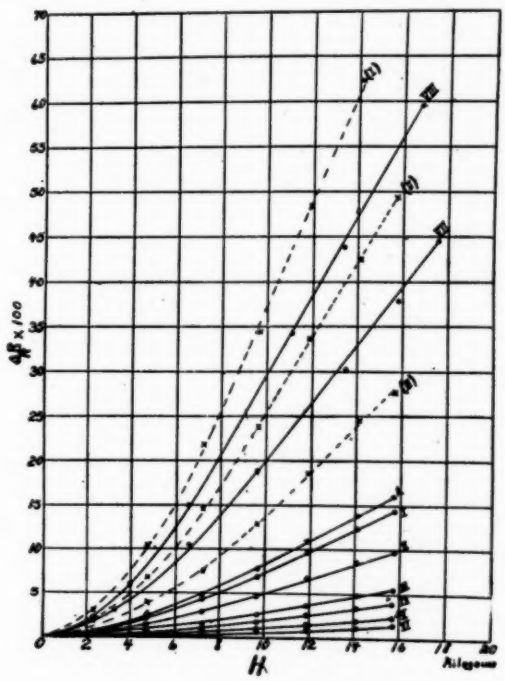

Fig. 4.

These curves represent the values of dr/r at various temperatures and values of the field for Film V–10.

out into practically straight lines. It is in this lower region that the "square law," proposed by Sir J. J. Thomson,[1] holds. As a check on the reproducibility of the results the data for Curve *I* were retaken immediately after taking the data for Curve *II*. The result is shown by the crosses (x) which practically coincide with the circles used to represent the initial data. Curve *A* was taken after Curve *VI* and also after a subsequent temperature-resistance run had been made with the film. The significance of the location of this curve will be discussed later in connection with evidences of aging in these films. The curves labelled (*I*), (*II*), and (*III*) were obtained by multiplying the ordinates

[1] J. J. Thomson, Rapports presentes au Congres International de Physique, 1900.

of the corresponding curves below by four. This has been done in order that it may be made plain that the form of the curves is the same throughout, so that the only effect of the change of temperature is to multiply the ordinates by a constant amount for any particular film. This is a rather significant and unexpected result. If we express the equation of the family of curves in terms of dr/r and some function of the field we may do so as follows:

$$dr/r = k\, f(H)$$

where k is a constant which depends on the temperature.

In Fig. 5 the effect of temperature is shown more directly for a similar film, V–9, where dr/r is plotted against the temperature for several

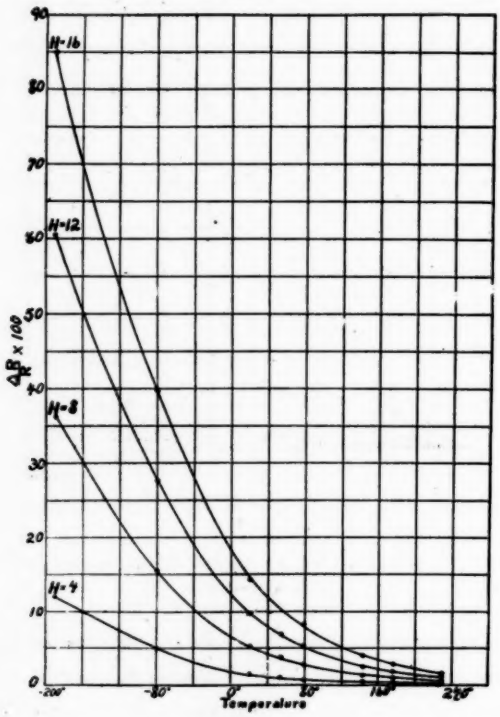

Fig. 5.

These curves, representing results obtained with Film V–9, shows directly the effect of temperature on the values of dr/r at a number of constant field strengths.

constant values of the field. Here again we see that as the temperature decreases the field produces correspondingly greater values of the increase of resistance. As in bismuth in bulk,[1] these curves indicate that the increase of resistance would vanish, or become very small, at least, at

[1] Drude and Nernst, Gött. Nachrichten, No. 14, p. 471, 1890.

the melting point of the metal. In form the curves are very similar to the curves representing the same quantities for bismuth in bulk. In fact, all measurements made on these films in the magnetic field support the statement that they differ mainly from solid bismuth in the magnitude of the changes produced by the field.

In order to give a basis for comparison of this series of films with those described in the previous paper (*loc. cit.*), in which the results were represented by plotting the percentage increase of resistance against the *square* of the field, a similar set of curves has been prepared for Film V–9. Since this film was of somewhat lower resistance than V–10, Fig. 4, it yielded larger values of dr/r under similar conditions. The result is shown in Fig. 6. It is quite evident that the values of dr/r are not directly proportional to the square of the field for these films as they seemed to be for those studied in the previous work. However, at the higher temperatures, *where the values of* dr/r *are small*, there seems to be an approach to such a proportionality for these films. This item is also quite in agreement with all previous work on this subject which has

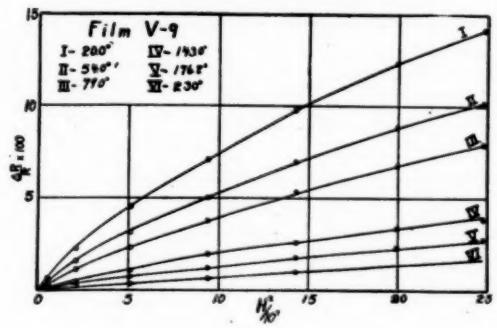

Fig. 6.

Data for Film V–9 showing that the values of dr/r are not proportional to the square of the field.

led to the conclusion that only where the effect of the field is small does the square law obtain,[1] and it seems to matter little as to what the cause of the smallness is, whether the nature of the substance or its condition. However, the result of this work tends to show that if the values of dr/r have been diminished by raising the temperature of a substance for which the square law did not hold at lower temperatures, it will also not hold at the higher temperatures. On the other hand there may be a limit above which the equation proposed in connection with the results shown in Fig. 4 does not hold, although at present there is no evidence of it within the range of temperatures here covered. It would be interesting

[1] S. C. Laws, Phil. Mag., 19, p. 685, 1910.

to study the behavior of bismuth in bulk in weak fields, up to 3 kilogauss, to determine whether this square law holds when the values of dr/r are small as a result of the low values of the field strength used for a substance which does not obey the law in stronger fields. Although the tendency has been to assume that it did hold in this region, as far as the writer is aware, special attention has never been given to measurements in very weak fields.

For a discussion of the dependence of the values of dr/r upon the thickness of the film, which can only be considered here in a qualitative way, the following series of films has been chosen:

Film V–14, — Resistance 54.88 ohms at 24.5°.
Film V–13, — Resistance 17.48 ohms at 21.0°.
Film V–10, — Resistance 10.54 ohms at 20.5°.
Film V– 9, — Resistance 7.07 ohms at 20.5°.

The corresponding data for these various films have been plotted in Fig. 7. Each curve was taken at the temperature given above in connection with the zero-field resistance of the film. These curves show

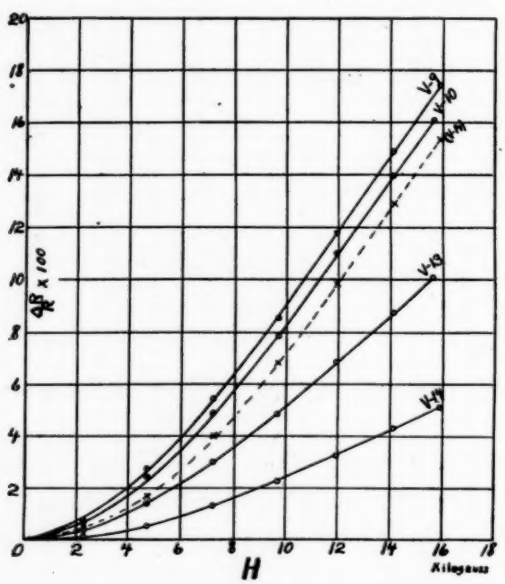

Fig. 7.

Curves showing the results for films of various thicknesses at room temperature.

that the films of lower resistance have a larger value of dr/r under similar conditions. This is rather to be expected since the thicker the film the closer the approach to solid bismuth. To show further that no essential change in the form of the curve occurs as the thickness of the film in-

creases, the ordinates for V–14 have been multiplied by three and replotted as indicated by the dotted curve which runs quite parallel to the neighboring curve for V–10. In Fig. 8 the similar results obtained for V–9, V–10, and V–14 at the temperature of liquid air are shown. Here the difference between V–9 and V–10 is much greater, indicating that the thicker films have a comparatively greater value of dr/r at the lower temperatures, a further evidence that in them the conditions are more nearly approaching those in solid bismuth.

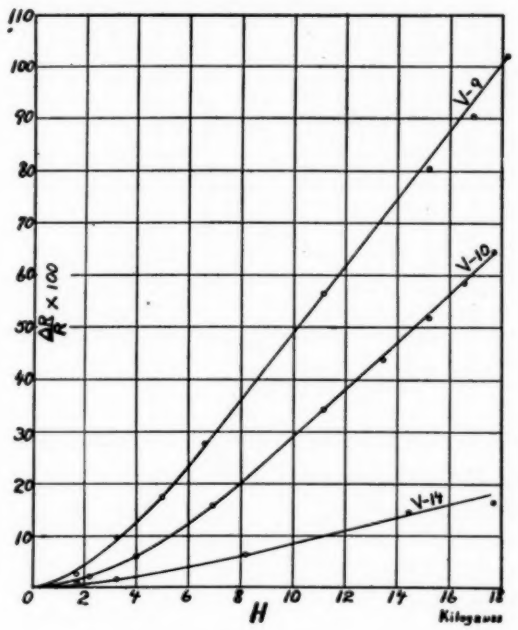

Fig. 8.

Showing the effect of thickness of the film upon the values of dr/r at the temperature of liquid air.

A discussion of the evidences of aging in these films and also of the form of the temperature-resistance curves may well be taken up together, since they are closely related. The temperature-resistance curves for Films V–14, V–13, V–5, and V–10 are shown in Figs. 9, 10, 11, and 12, respectively. In Fig. 9 we have a typical curve for a film of higher resistance. It is to be noted that the first cooling curve is exactly retraced by the second heating curve and the second cooling curve, whereas the first heating curve lies somewhat above these three. The explanation for this behavior is evident when attention is called to the fact that, as shown by the curves, care was taken in making the second heating not to exceed the previous maximum temperature for the first heating.

Hence no further aging occurred during the second heating and the resistance remained unchanged. This plainly shows that this film had not had its aging process carried to the limit before the temperature-

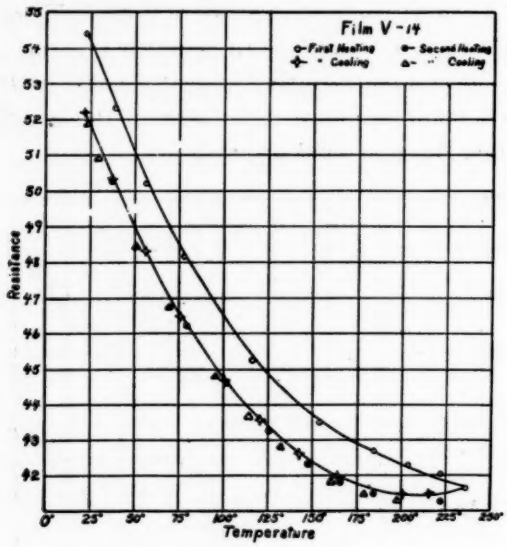

Fig. 9.

resistance measurements here shown were undertaken, and that in making the first heating the previous maximum temperature to which the film had been heated was exceeded with a resultant decrease in resistance

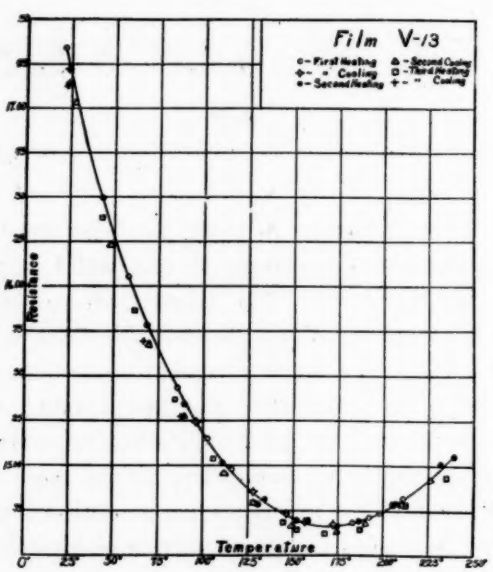

Fig. 10.

of the film. One would expect then that this would show itself in the behavior of the film in the magnetic field. Data taken in the magnetic field before and after these temperature-resistance measurements yielded

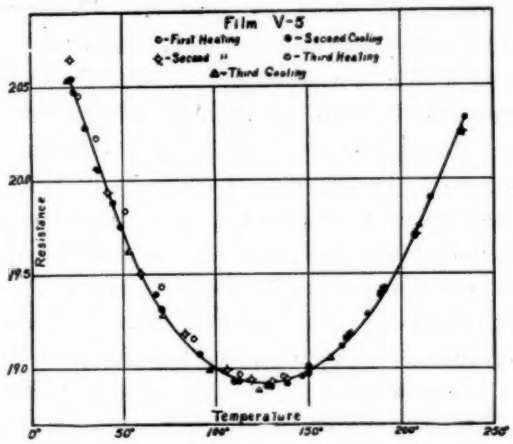

Fig. 11.

the expected result. Since too many figures would be required to show all the results in detail, an idea of the relative magnitude of this change produced in the values of dr/r may be obtained by reference to Fig. 4,

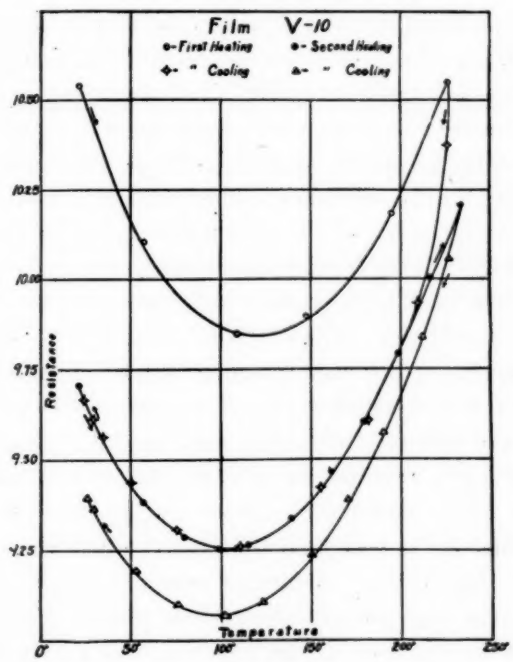

Fig. 12.

The above figures show typical temperature-resistance curves for films of different thickness.

where the similar results for Film V–10 are represented. The curves labelled *I* and *A* show the behavior of this film when treated in a like manner. Curve *I* was taken before the temperature-resistance run and Curve *A* afterwards at the same temperature. The result of the aging was, as shown, to increase the values of dr/r. A further point of interest in Fig. 9 is the suggestion of a minimum value of the resistance at about 210°. This minimum shows much more clearly in the curve for Film V–13 in Fig. 10. It occurs, moreover, at a lower temperature, in the neighborhood of 170°. In this connection it is to be noted that V–13 has a considerably lower resistance than the preceding film. Furthermore the preliminary heat treatment was carried out much more thoroughly, the results of which are strikingly shown by the reproducibility of the data. The observed points are here indicated by various symbols for three heatings and three coolings, taken over a period of several days, and yet a single curve represents all fairly well; only the very slightest traces of aging are to be detected. Likewise it was found possible to reproduce the measurements in the magnetic field with similar accuracy for this film. These results are quite contrary to any of the author's previous experiences with sputtered films. In fact, it had always been found impossible to so age a film that its resistance would remain constant for more than a few hours at room temperature, while exposed to the air, and reproducible measurements at higher temperatures were out of the question. To show more completely the form of the temperature-resistance curve the data for Film V–5 are shown in Fig. 11. Here both branches of the curve, which is perfectly symmetrical and in form approaches that of a parabola, are well defined. This film also has been thoroughly aged and the minimum resistance has shifted to a still lower temperature. An attempt to fit a parabolic equation to this curve has been made. Although the deviations are slight, they seem to be somewhat greater than possible experimental errors. All previous films of bismuth which have been studied by the author, or by others, so far as a search of the literature has revealed, have without exception had negative temperature coefficients of resistance. We have here, however, an example where the coefficient, initially negative at room temperature, actually reverses its sign as the film is heated and becomes positive. The maximum value of the positive coefficient which has been obtained is far less than that for bismuth in bulk, roughly of one quarter the magnitude. A further example of this form of curve is shown in Fig. 12, representing the results obtained with Film V–10. This is another example of a film that has been only partially aged, hence there was a big decrease in resistance as the film was heated for

the first time. The effect of the second heating, as was to be expected, was considerably less, although it was carried out to a slightly higher temperature. The symmetry of the curves is considerably distorted by this aging effect which takes place at the higher temperatures. It is to be noted that the points representing the second heating lie closely on the curve for the first cooling, until the higher temperatures are reached, showing that the aging occurs chiefly at temperatures above 200°.

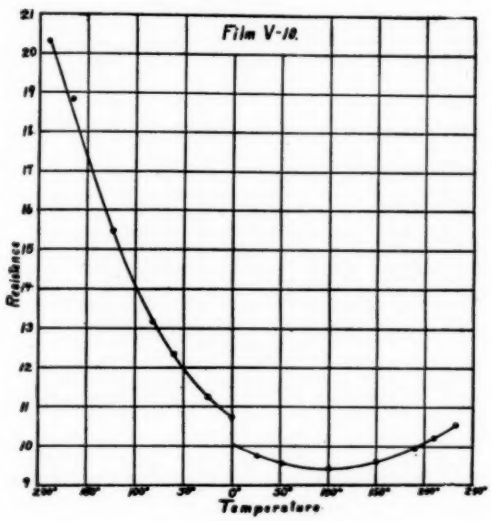

Fig. 13.

Showing the complete temperature resistance-curve for Film V–10.

In Fig. 13 the complete temperature-resistance curve for Film V–9 is represented. The part from room temperature to 230° was taken some months before the part at low temperatures. This fact, together with the effect of increased pressure to which the film was subjected when air was admitted to it, accounts for the jog in the curve at 0°. If the part taken at the higher temperatures were raised throughout by a constant amount, equal to the difference of ordinates at 0°, the two parts would then form a smooth curve which agrees in form with those taken for other films throughout this range of temperatures. Hence there seems to be no evidence of any peculiarities in the low temperature part of the temperature-resistance curves for these films.

To show what happens to one of these films when it is heated in contact with the air, a temperature-resistance run for Film V–8 is shown in Fig. 14. This film was prepared in the usual way and during the first heating and cooling behaved much the same as had all previous films which were thoroughly aged, the two sets of observations lying along the

same curve. However, soon after the beginning of the second heating, the resistance began to increase rapidly. After cooling down it had a considerably higher resistance than before at room temperature. This anomalous behavior was hard to explain until the film was taken out of the bath and examined. It was then discovered that a yellowish coating of oxide had form on the surface, indicating that the glass tube had given

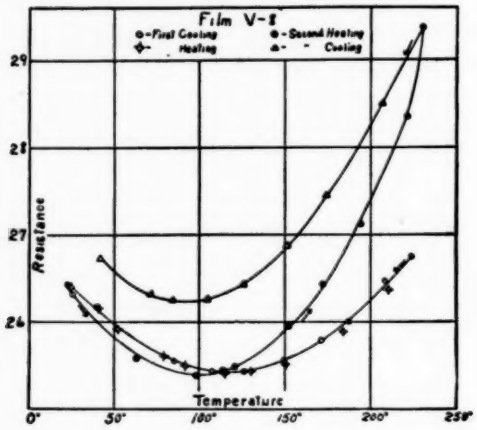

Fig. 14.

This figure shows the temperature-resistance curve obtained for Film V–8, which was attacked by the air as a result of a break in the protecting tube.

way at some point, admitting air. On further examination this proved to be the case. There seems to be an additional effect of the air on the form of this curve beyond that produced by oxidation alone, however. The difference in ordinates at the maximum temperature is considerably greater than at room temperature, hence the increase of resistance at the higher temperature is not all permanent, as it would be if it were due solely to oxidation. This additional effect may well be caused by the pressure, although this point was not specially investigated.

The foregoing covers the experimental results of this investigation. As far as the magnetic measurements are concerned little more can be said beyond the mere statement that these films approach the behavior of bismuth in bulk, the approach being nearer the thicker the film. Any theoretical discussion of these results and interpretation in terms of the electron theory would necessarily follow the same general lines as those for bismuth in bulk. Too little is known at present with any degree of certainty about the nature of electrical conduction in metals to enable very much progress to be made in this direction beyond what has already been accomplished by Thomson and others. This is very clear when

attention is called to the fact that the most successful theories so far advanced,[1] either agree with the experimental data only for very limited ranges of the field strength, or require properties which bismuth does not possess, *e.g.*, magnetostriction.

It is also difficult to explain successfully the form of the temperature-resistance curves of these films. One explanation which might be offered for the reversal of the sign of the temperature coefficient and the consequent minimum resistance, the location of which varies from film to film, and is, in general, at a lower temperature the lower the resistance of the film, is as follows: It is based on the fact that the metal particles have a larger coefficient of thermal expansion than the glass. Hence as the film rises in temperature they expand more rapidly and bring more particles into contact, reducing the negative temperature coefficient of resistance, and finally, if the film is thick enough, the particles are crowded close enough together and at a rate fast enough to reduce this coefficient to zero, then finally to reverse its sign. Then the metallic film begins to behave somewhat like the metal in bulk, but is prevented from attaining a positive coefficient as large as that for solid bismuth by the fact that the glass also continues to expand, thus preventing the compacting process from going far enough to establish contact between all the possible particles. The study of this phase of the subject is limited by the comparatively low melting point of bismuth (about 260°). This explanation is far from satisfactory, however, since on the basis of it a platinum film sputtered on glass should have practically a zero temperature coefficient, which is contrary to the facts as reported by other observers. But then there must be taken into account also the effect of temperature on the conductivity of the metallic particles themselves. Hence we have at least two influences which must be considered simultaneously. The first is that due to the difference in the thermal coefficients of expansion which should cause an increase or decrease in the number of possible paths for electrons from particle to particle, according as the film is heated or cooled. The second is that which results from the effect of temperature upon the motions of the electrons within the particles, and also its effect upon the ease with which an electron may detach itself from one particle and move on to the next. This view of the structure of the films is strengthened by the fact that x-ray studies[2] of the films indicated that they were composed of small crystals of metal, with random orientation, which have been detached from the cathode and deposited on the glass during sputtering. This view is in contrast

[1] E. P. Adams, PHYS. REV., 24, p. 248, 1907.

[2] H. Kahler, PHYS. REV., 17, p. 230, 1921.

with the evaporation theory which holds that the metal of the cathode is vaporized and then condenses on the glass, in which case a film of entirely different structure from that of the cathode metal might result. However, this point is not settled.

For further comparison of the results here given with those obtained for bismuth in bulk, a reference to an investigation by Dr. F. C. Blake[1] is included. His work, published in 1909, covers practically the same range for the solid metal.

SUMMARY.

The preceding results may be summarized as follows:

1. By protecting sputtered bismuth films in a vacuum and heating them to temperatures near the melting point of bismuth it is possible to develop the property of an increase of resistance in a magnetic field to about one fifth that possessed by bismuth in bulk.

2. The higher the temperature of the film the smaller the value of the percentage increase of resistance for a given field.

3. The form of the curve between dr/r and field strength is independent of the temperature of these films, *i.e.*, $dr/r = kf(H)$.

4. The temperature-resistance curves for these films are parabolic in form, and the minimum resistance is at a lower temperature the thicker the film.

5. If these films have been subjected to a very thorough heat treatment the temperature-resistance curve is fixed and definite. Under these conditions reproducible data are easily obtained in the magnetic field.

6. If the film is only partially aged it *decreases* in resistance with continued heating and exhibits correspondingly greater values of dr/r in the magnetic field as a result of the heating.

In conclusion I wish to thank Professors Ernest Merritt and F. K. Richtmyer, under whose direction this work was done, and all others, who, by advice or suggestions, have helped the progress of this investigation.

PHYSICAL LABORATORY,
CORNELL UNIVERSITY.

[1] F. C. Blake, Ann. d. Phys., 28, p. 449, 1909.

CONDUCTIVITY OF FLAMES CONTAINING SALT VAPORS.

By A. B. Bryan.

Synopsis.

Conductivity of a Flame Sprayed with Salt Solutions, as a Function of the Concentration.—The method used is due to H. A. Wilson. The ratio of the potential gradients in the central parts of two flames, each about 7 cm. wide, through which the same current was passed, was determined by means of a quadrant electrometer connected alternately to each of two pairs of probe wires in the flames, by means of a rotating commutator. Both flames were sprayed with identical sprayers. When desired for greater sensitiveness the current through the flames could be increased by applying K_2CO_3 to the cathodes. Using the conductivity produced by distilled water as a standard, the relative conductivities of various concentrations of *potassium carbonate, sodium carbonate, cæsium chloride, calcium chloride, barium chloride, aluminium chloride and boric acid* were determined. For the last four the conductivity was found to be approximately proportional to the cube root of the concentration, whereas in the case of the others the relation is more complicated. A *theory* to account for the cube root relation is suggested. The conductivities due to *mixtures of two solutions* were found to agree with the values computed from the conductivities due to the components alone. *Uranium nitrate* gave little or no conductivity.

I. Introduction.

THE first extensive investigation of the electrical conductivity of flames containing salt vapors was made by Arrhenuis[1] in 1890. He used a vertical flame with carefully regulated air and gas supplies and measured the current between two platinum electrodes in the flame with a constant potential difference, taking this current as a measure of the conductivity. A sprayer was arranged to spray a salt solution into the flame with the air supply and the effect of the salt on the conductivity could thus be measured.

Arrhenius made experiments with salts of the alkali metals, alkaline earth metals and some of the heavier metals, such as copper, zinc, iron and aluminium. For the alkali metals, all salts of each metal were found to give the same conductivity, and this conductivity was proportional to the square root of the concentration of the solution used. The conductivities for the different alkali metals were found to increase with the atomic weight. For the alkaline earth metals, no measurements were made on the variation of conductivity with concentration. The heavier metals were found to give little if any conductivity. The values obtained with them were all so small as to fall within the limits of experi-

[1] Wied. Ann., Vol. xliii., p. 18, 1891.

mental error. For a mixture of two alkali metal salts (sodium and potassium sulphate or chloride), the conductivity produced was found to be greater than that produced by either of the two salts separately but less than the sum of the two.

Other measurements of the conductivity produced by salt vapors in flames have been made by A. Smithells, H. M. Dawson and H. A. Wilson.[1] The apparatus used by them was similar to that used by Arrhenius and they also found that for the halogen salts of the alkali metals, the conductivity was proportional to the square root of the concentration. For the oxysalts this was not true, except at very small concentrations.

The electrical conductivity of flames has also been measured by H. A. Wilson.[2] He found that for large concentrations, the conductivity produced by salts of alkali metals was proportional to the square root of the concentration used and independent of the nature of the acid radical, so long as solutions having equal numbers of metal atoms per cubic centimeter were used. Wilson's experimental method, which has several advantages over that used by Arrhenius, has been used in the present work and will be fully described later.

In this paper additional data will be presented on the conductivity produced by salts of the alkali metals sodium, potassium and cæsium and various mixtures of the same, and by calcium, barium and aluminum chlorides, boric acid and uranium nitrate.

II. Experimental Method.

The apparatus used in this experiment is in all essentials similar to that used by H. A. Wilson. Two similar burners were used (*A* and *B*, Fig. 1), each consisting of a row of eight short quartz tubes set in a horizontal brass tube (*bb*) with De Khotinsky cement. The quartz tubes were of approximately 0.5 cm. internal diameter. In each flame were two electrodes (*EE*) of thin sheet platinum, 1.5 cm. square and 6.5 cm. apart, and two horizontal platinum wires (*WW*) 2.5 cm. apart. The electrodes in the two flames were connected directly in series with a battery (B_5)

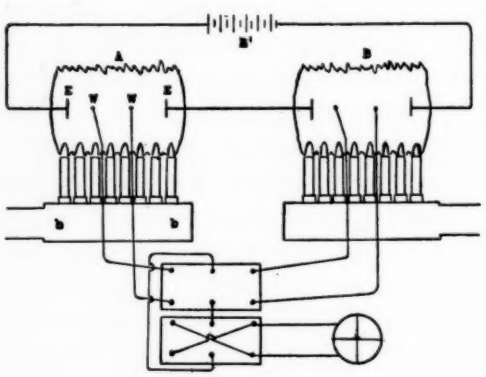

Fig. 1.

[1] Phil. Trans., A, Vol. 193, p. 89, 1900.

[2] Phil. Trans., A, Vol. 216, p. 63.

of 15 volts, so that the same current passed through both flames. No current measuring instrument of any kind was used. The wires (*WW*) in both flames were connected through a commutator and reversing key to the quadrants of a quadrant electrometer, in such a manner that either pair of wires could be connected to the electrometer in turn. A rather heavy quartz fiber electrometer suspension was used. The needle of the electrometer was continuously connected to a source of potential, usually about 86 volts, and the sensitivity of the electrometer with this potential on the needle was 52 mm. per volt. The electrodes (*EE*), the wires (*WW*) and the battery (*B'*) were all supported on ebonite rods which afforded good insulation. The electrometer was insulated on ebonite blocks and its case was connected to one pair of quadrants. The commutator and reversing key were made of paraffin blocks.

Each burner was connected to a sprayer which sprayed a solution into the flame. Fig. 2 shows one of the burners connected to its sprayer

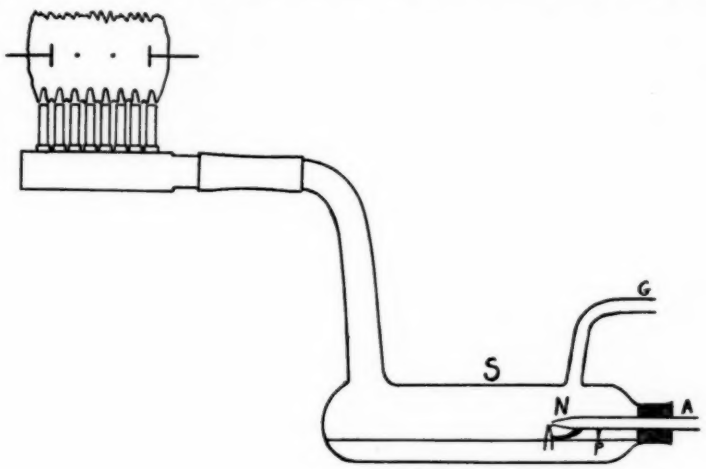

Fig. 2.

with a short piece of large rubber tubing. Gasoline gas was admitted at *G* and air at *A*. The air supply, taken from the compressed air mains of the building, was maintained at constant pressure by allowing part of it to escape through a mercury trap and by passing it through two large carboys in series to remove small fluctuations. The air pressure was measured with a water manometer. Connections to the two sprayers from the common air and gas supplies were made with equal lengths of large rubber tubing, so that the air and gas pressures, respectively, at the two sprayers were the same. It was not found practicable to maintain the gas pressure constant from day to day, due to the varying

quality of the gas, and so the practice was to adjust the gas pressure each time to get equal non-luminous flames with well defined cones. The spraying nozzle (N) was fixed into the body of the sprayer through a rubber stopper and was held firmly by supports outside the sprayer, since it was found that if the nozzle tilted up very slightly toward the gas inlet the flow of gas was greatly increased due to the "injector" action of the stream of air. A small glass point (P) was fixed to the nozzle to mark the level to which the sprayer was always filled with solution. The two sprayers were made as nearly alike as possible and the nozzles were adjusted to deliver almost equal amounts of liquid and of air per second on equal air pressures. The sprayers were tested and it was found that sprayer A required 8.6 c.c. to refill after going 40 minutes, while sprayer B required 8.4 c.c. to refill after the same time. Sprayer A required 4.4 c.c. to refill after going 20 minutes, roughly half as much as before, indicating that the rate of delivery of solution to the burners is uniform and not much affected by the lowering level of solution in the sprayer during a long period of time. The air supplies were found to be equal to within one per cent. But it is not necessary that the two sprayers be exactly alike and is not necessary to assume that they deliver equal amounts of solution. A conical hood was fixed above each flame and connected to a suction pump to remove the flame gases and salt vapors and prevent their escape into the room.

The method of measuring conductivities with this apparatus will now be explained. Flame A serves merely as a standard with which the conductivity of flame B is compared, thus making it possible to obtain the conductivities of various solutions in B relative to one another. The conductivity of flame B is taken as unity when its sprayer is spraying distilled water. The electrometer is alternately connected, by means of the commutator, to the wires EE in flame A and to those in flame B, and the ratio R of the electrometer deflection for flame A to that for flame B is determined. Since the electrometer deflection is inversely proportional to the conductivity of the flames, R will be inversely proportional to the conductivity of flame B when that of flame A is kept constant. Hence if the ratio of the deflections is R_1 with water only in B and R_2 with a salt solution in B, the solution in A being the same in each case, then R_2/R_1 will be equal to the conductivity of flame B with the salt solution in it, since the conductivity of B is taken equal to unity when only water is in it. To get accurate results it is necessary to keep the ratio R less than three and greater than one third. To do this when solutions of increasing concentration are used in B it is necessary to increase the concentration of the solution in A. When the

solution in A is changed the same solution must be kept in B for two readings, in order that the conductivity of the new standard may be determined. To illustrate the procedure a number of readings are given in Table I. below, whereby the conductivities of a number of CsCl solutions were determined. Under A and B are given the solutions which were sprayed into flames A and B respectively. Under R are given the ratios of electrometer deflections for flame A to those for flame B. Column C_A gives the conductivities of flame A. These values are given for convenience in calculation only and must not be taken as the true conductivities for the various solutions. In column C_B are given the true conductivities for the solutions which have been used in flame B. The concentrations of the solutions are given in grams per liter.

TABLE I.

A	B	R	C_A	C_B
13.001 K_2CO_3	H_2O	.806	1.24	1.0
.001 K_2CO_3	.004 CsCl	2.19	1.24	2.72
.05 K_2CO_3	.004 CsCl	.288	9.44	2.72
.05 K_2CO_3	.04 CsCl	1.30	9.44	12.25
.05 K_2CO_3	.04 CsCl + .10 K_2CO_3	2.63	9.44	24.8
2.00 K_2CO_3	.04 CsCl + .10 K_2CO_3	.33	74.4	24.8
2.00 K_2CO_3	.40 CsCl	.739	74.4	55.0
2.00 K_2CO_3	4.00 CsCl	2.09	74.4	155.5

The advantages of this experimental method will now be considered. The potential along a flame was found by H. A. Wilson to fall in the way shown in the curve in Fig. 3, which is taken from his paper.[1] There

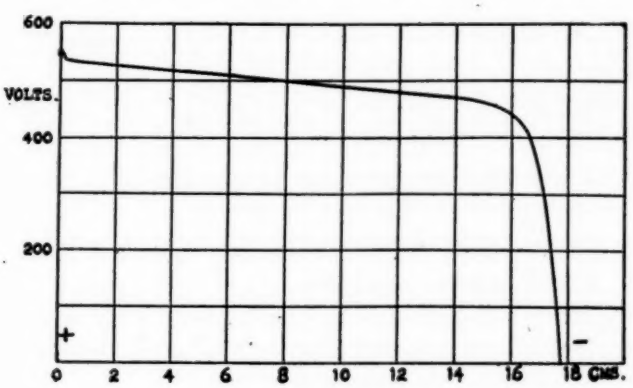

Fig. 3.

[1] Proc. of the Phys. Soc. of London, Vol. xx., p. 476.

is a slight drop at the positive electrode, then a uniform gradient through the greater part of the flame's length and finally a very large drop close to the negative electrode. The total potential difference is 550 volts and of this there is a drop of 450 volts within one centimeter of the cathode. The relation between potential and current may be represented by the equation,

$$V = ACd + BC^2. \qquad (1)$$

The term BC^2 represents the potential drops at the electrodes and is usually much larger than the ACd term, especially if the electrodes are close together. Thus if only two electrodes are used in the flame and the value of C/V is taken as a measure of the conductivity of the flame, as was done by Arrhenius, this value will not be constant but will decrease as the current is increased. But if the potential difference between two points in the middle of the flame, away from either electrode, is used, then the value of C/V will be independent of C and will furnish a better measure of the flame's conductivity, since Ohm's Law holds in the center of the flame. This is what is done in the method just described. The potential difference between the wires EE was measured with an electrostatic instrument so that no current was taken from the flame and the manner in which the potential falls along the flame was not changed by the presence of the wires.

It would be possible to measure the current through the flame directly and use the ratio of this current to the potential difference between the wires EE as a measure of the flame's conductivity, but there are several objections to this. It is difficult to keep the air and gas supplies, the electrometer sensitivity and all other conditions absolutely constant for any length of time, and so what is done instead is to put the flame A in series with flame B and use it as a standard for comparison. Then any changes affecting flame B will affect A equally and the ratios will not be changed.

The current through a flame can be greatly increased by applying K_2CO_3 to the cathode. The vaporizing K_2CO_3 will make the resistance of the flame very small in the space next to the cathode and since a large part of the flame's total resistance is in this space, as may be seen from Fig. 3, the total resistance will be decreased by a large percentage and the current correspondingly increased. It was frequently necessary to increase the current in this way in the present work in order to get electrometer deflections large enough to be read accurately. CaO, obtained by coating the cathodes with sealing wax and then heating them, was sometimes used instead of K_2CO_3.

III. Results.

In Table II. below are given the conductivities for solutions of several concentrations of K_2CO_3, Na_2CO_3, and CsCl.

Table II.

Solution Sprayed.	Conductivity.
.01 K_2CO_3	5.52
.10 "	22.9
1.00 "	77.7
10.00 "	225.0
.005 Na_2CO_3	1.69
.02 "	3.31
.10 "	6.36
1.0 "	14.55
10.0 "	37.7
50.0 "	75.0
.004 CsCl	2.72
.04 "	12.25
.4 "	55.0
4.0 "	155.5

The values for K_2CO_3 and Na_2CO_3 are averages of a number of readings. These averages were taken in the following way. A number of sets of readings such as that given in Table I. were taken and from each of these sets a value was obtained for the ratio of the conductivity for .01 K_2CO_3 solution to that for water. The average of these ratios was used to calculate the conductivity for .01 K_2CO_3, assuming the conductivity for water to be unity. Similarly a value was obtained from each set of readings for the ratio of the conductivity for 0.10 K_2CO_3 to that for .01 K_2CO_3, and the average of these ratios was used to calculate the conductivity for the .10 K_2CO_3 solution, and so on. This method of averaging prevents an error in the first part of a set of readings from affecting all the later values. In Table III. are given the values of these ratios for different solutions of K_2CO_3. Those numbers marked with asterisks are omitted in taking the averages. For the others the average variation from the mean values is about four per cent. This gives a fair idea of the accuracy of the results.

According to the theory given by H. A. Wilson[1] for the electrical conductivity of flames containing salt vapors, the relation between the conductivity C and the concentration K of salt solution sprayed is given by the equation,

[1] Phil. Trans., A, Vol. 216, p. 79.

TABLE III.

$\frac{.01\ K_2CO_3}{H_2O}$	$\frac{.10\ K_2CO_3}{.01\ K_2CO_3}$	$\frac{1.00\ K_2CO_3}{.10\ K_2CO_3}$	$\frac{10.\ K_2CO_3}{1.\ K_2CO_3}$
4.48*	3.52*	3.85*	2.85
5.22	4.46	3.64	2.84
5.85	5.85*	3.27	2.53*
5.36	4.39	3.31	2.87
5.42	4.09	3.29	3.01
5.75	3.83		
	4.02		
5.52	4.16	3.38	2.89

$$\frac{10^4 KC}{C^2 - 1} = b + aC, \qquad (2)$$

where a and b are constants. When C is large so that bC may be neglected in comparison with aC^2, then the above equation may be written,

$$10^4 K = aC^2. \qquad (3)$$

That is, the conductivity is proportional to the square root of the concentration, as was found to be approximately true by both Arrhenius and H. A. Wilson.

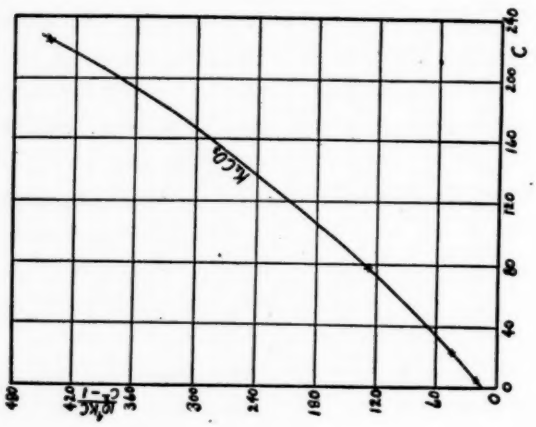

Fig. 4.

When $(10^4 KC/(C^2 - 1))$ is plotted against C, a straight line should be given according to equation 2. In Figs. 4, 5 and 6 are given these curves, plotted for K_2CO_3, Na_2CO_3 and CsCl. They are not straight lines but are all slightly concave upward, indicating that the theory as given by Wilson does not accurately fit the experimental results. It has been found empirically that C is approximately a linear function of $K^{.435}$. In Figs. 7, 8 and 9, C is plotted against $K^{.435}$ for the data in

Table II. and it will be seen that a good straight line is given in each case. Hence the relation between concentration and conductivity may be expressed by the equation,

$$K^{.435} = AC + B, \tag{4}$$

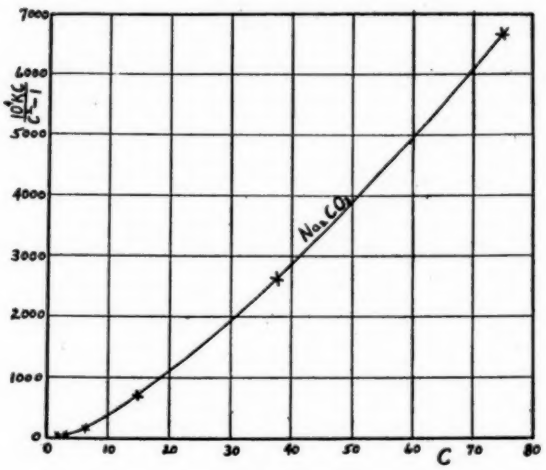

Fig. 5.

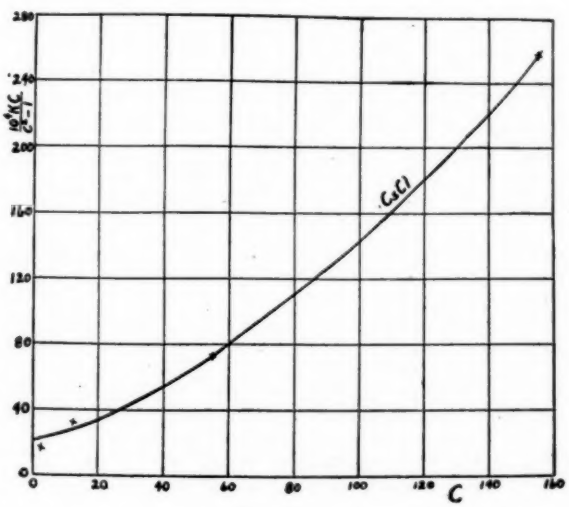

Fig. 6.

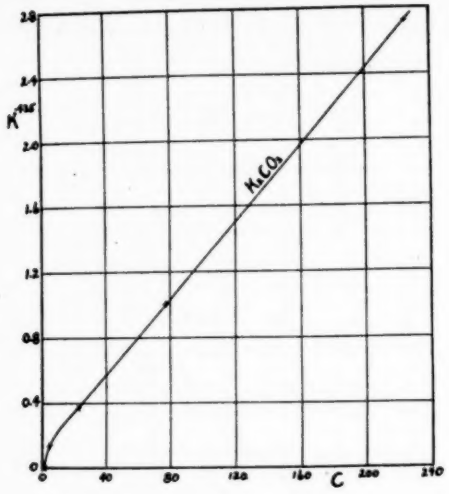

Fig. 7.

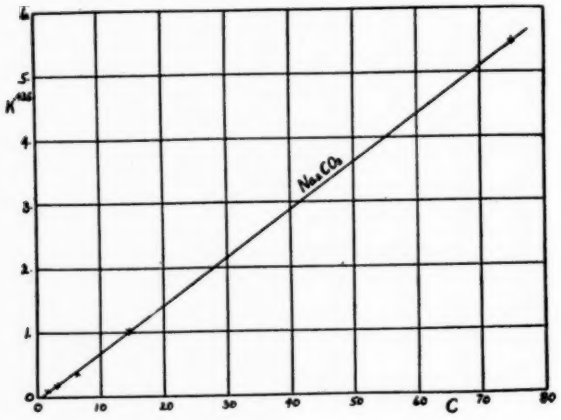

Fig. 8.

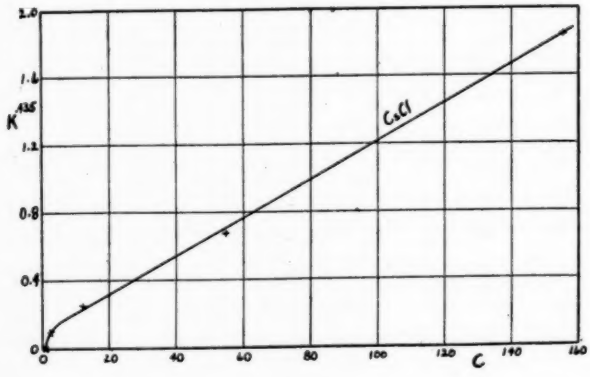

Fig. 9.

where A and B are constants. This equation holds for the larger conductivities only. For the smaller values the relation between C and $K^{.435}$ is not linear and an equation of the form,

$$K^{.435} = (C - 1)\left(A + \frac{B}{C^n}\right) \tag{5}$$

will better fit the experimental curves.

In Table IV. are given the experimentally determined and the calculated conductivities for several mixtures of salts.

TABLE IV.

Solution Sprayed.	Experimental Conductivity.	Calculated Conductivity.
0.1 K_2CO_3 + 1.0 Na_2CO_3	27.1	26.2
0.1 " + 10.0 "	40.2	42.6
1.0 " + 10.0 "	85.0	83.6
1.0 " + 20.0 "	88.1	88.1
0.1 " + 0.04 CsCl	24.8	25.1
0.1 " + 0.1 "	33.5	33.5
1.0 " + 0.4 "	89.7	91.2
1.0 " + 1.0 "	115.0	109.5

The following equation is also given by H. A. Wilson[1] to represent the relation between conductivity and concentration when a mixture of two salts is used.

$$\frac{C^2 - 1}{C} = \frac{10^4 K_1}{b_1 + a_1 C} + \frac{10^4 K_2}{b_2 + a_2 C}, \tag{6}$$

where K_1 and K_2 are the numbers of grams of the two salts in a liter of the solution which produces a conductivity C. a_1, b_1, a_2 and b_2 are constants depending on the salts used. When C is large b_1 and b_2 may be neglected and the equation may be written:

$$C^2 = \frac{10^4 K_1}{a_1} + \frac{10^4 K_2}{a_2}. \tag{7}$$

But from equation (3),

$$\frac{10^4 K}{a} = C^2,$$

when a single salt is used, and therefore, if C_1 and C_2 are the conductivities for concentrations K_1 and K_2 of two salts taken separately, then

$$\begin{aligned} C^2 &= C_1^2 + C_2^2, \\ C &= \sqrt{C_1^2 + C_2^2}. \end{aligned} \tag{8}$$

This equation could be used to calculate what the conductivity due to a mixture of two salts should be, knowing the conductivities which the two salts produce separately. But since in the present work C has been

[1] Phil. Trans., A, Vol. 216, p. 87.

found to be more accurately proportional to $\sqrt[2.3]{K}$ than to $\sqrt{K}$ for large concentrations, a more accurate formula will be,

$$C = \sqrt[2.3]{C_1^{2.3} + C_2^{2.3}}. \quad (9)$$

This formula has been used to obtain the calculated values of conductivity in Table IV. above. It will be seen that the agreement between experimental and calculated values is fairly good in every case.

The conductivity was also measured for several concentrations of $CaCl_2$ solution. The curve in Fig. 10 shows the results obtained. At concentrations of above 15 grams per liter a white deposit of oxide is formed on the electrodes and burner tubes. The whole flame is itself filled with small particles. This was shown by passing a beam of sunlight through the flame. The path of the beam through the flame could be seen on account of the light scattered by the small particles and this scattered light was found to be polarized.

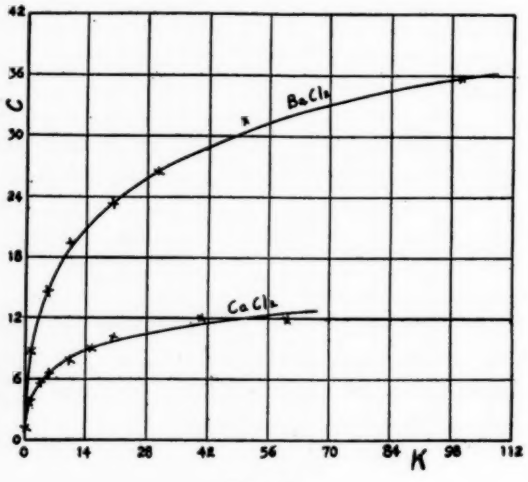

Fig. 10.

A $CaCl_2$ solution was found to make the most satisfactory standard solution for flame *A* because the oxide deposit produced on the electrodes kept down the potential drop at the cathodes and did not require renewal, as was the case when K_2CO_3 or lime was used on the cathodes.

The curve obtained for $BaCl_2$ is also shown in Fig. 10. It is seen that at a given concentration $BaCl_2$ gives about twice as much conductivity as $CaCl_2$. $BaCl_2$ does not produce any noticeable deposit on the electrodes.

If (log *K*) is plotted against (log *C*) for $BaCl_2$ and $CaCl_2$ as in Fig. 11, straight lines are obtained and from the slopes of these lines it is found that the conductivity is roughly proportional to the cube root of the

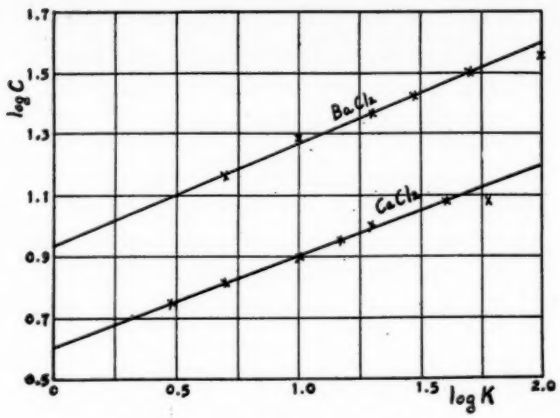

Fig. 11.

concentration. The following theory for this variation of C with K was worked out as the result of a suggestion by Professor H. A. Wilson.

The solution is sprayed into the flame in minute drops, each of which evaporates and leaves a small, non-volatile, salt particle as it enters the flame. The number of drops entering the flame should depend only on the sprayer and should be independent of the concentration of the solution. Hence the number of particles per cubic centimeter in the flame, formed by the evaporation of small drops of solution, should be constant. But the volume of each of these particles should be proportional to the concentration of the solution used. These particles will emit electrons and become positively charged.

Let N = number of positively charged particles per cubic centimeter in the flame.

r = radius of one of these particles.

E = the positive charge on each particle.

n = number of electrons per cubic centimeter which come from the salt particles.

m = number of electrons per cubic centimeter which are produced by ionization of flame gas molecules.

F = number of flame gas molecules per cubic centimeter capable of being ionized.

k = velocity of an electron in unit electric field.

The rate of emission of electrons by the positive particles in one cubic centimeter will be proportional to N and to the surface area of each particle, or equal to $BN4\pi r^2$ where B is a constant.

The electric intensity at a distance d from a positive particle will be E/d^2. The rate of absorption of electrons by a positive particle

will be equal to $\{E/d^2 \cdot k4\pi d^2(n+m)\}$. The rate of absorption per cubic centimeter will therefore be $\{NEk4\pi(n+m)\}$ and must be equal to the rate of emission when a state of equilibrium is reached. Therefore,

$$NEk4\pi(n+m) = BN4\pi r^2, \tag{10}$$

$$r^2 = \frac{Ek(n+m)}{B}.$$

Since the total positive charge on the particles in a cubic centimeter must be equal to the total negative charge on the electrons which have been emitted by these particles, we have,

$$NE = ne,$$

where (e) is the charge on one electron,

$$E = \frac{ne}{N},$$

$$r^2 = \frac{nek}{NB}(n+m),$$

$$n = \frac{Ar^2}{(n+m)},$$

where

$$A = \frac{NB}{ek}. \tag{11}$$

The rate at which electrons are produced by ionization of the flame gas molecules is proportional to F. The rate at which electrons are lost through recombination with the flame gas positive ions is proportional to the number of these ions m and to the number of electrons per cubic centimeter. Since the rate of production must be equal to the rate of recombination when a state of equilibrium is reached, we have,

$$F = \beta m(n+m),$$

$$m = \frac{F}{\beta(n+m)}, \tag{12}$$

where β is a constant. Adding (11) and (12), we have,

$$n + m = \frac{Ar^2\beta + F}{\beta(n+m)},$$

$$n + m = \sqrt{Ar^2 + \frac{F}{\beta}}. \tag{13}$$

As has been said, the volume of a particle must be proportional to the concentration of the solution, or

$$\frac{4}{3}\pi r^3 \propto K,$$

$$r^2 \propto K^{2/3},$$

where K is the concentration in grams per liter. Then (13) becomes.

$$n + m = \sqrt{A_1 K^{2/3} + \frac{F}{\beta}}, \tag{14}$$

where A_1 is a new constant.

We assume that the positive particles are so heavy that they remain practically stationary and the electrons carry all the current. The conductivity C will be proportional to the total number of electrons per cubic centimeter.

$$C = A_2(n + m).$$

Substitute for $(n + m)$ from (14),

$$C = A_2\sqrt{A_1 K^{2/3} + \frac{F}{\beta}}. \tag{15}$$

Now assume $C = 1$ when $K = 0$, that is, when there is no salt in the flame. Then (15) becomes,

$$1 = A_2\sqrt{\frac{F}{\beta}},$$

$$\frac{F}{\beta} = \frac{1}{A_2^2}.$$

Substitute this value back into (15),

$$C = A_2\sqrt{A_1 K^{2/3} + \frac{1}{A_2^2}},$$

$$C^2 - 1 = A_3 K^{2/3}, \tag{16}$$

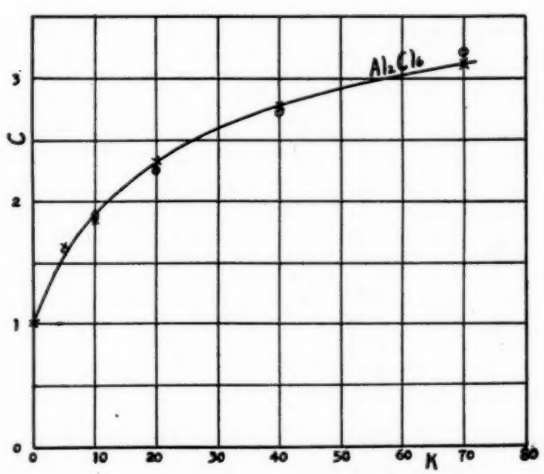

Fig. 12.

between conductivity and concentration. When C is large compared with one, the conductivity is directly proportional to the cube root of the concentration, as was observed for $CaCl_2$ and $BaCl_2$. No measure-

where A_3 is a new constant. This equation gives the final relation

ments were made with very small concentrations of these salts and consequently the above equation cannot be further tested with the data on $BaCl_2$ and $CaCl_2$.

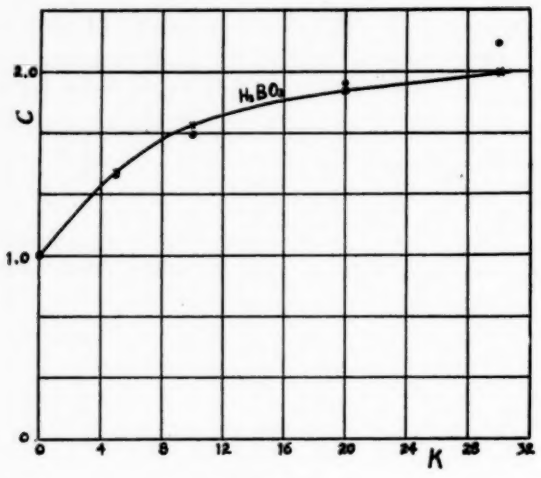

Fig. 13.

In Figs. 12 and 13 are shown curves obtained for Al_2Cl_6 and H_3BO_3. These curves may be used to test equation (16) because for these two salts the conductivities are small. The crosses in Figs. 12 and 13 indicate the experimental points.

TABLE V.

Al_2Cl_6			H_3BO_3		
K	C	A_3	K	C	A_3
5.0	1.63	0.568	5.0	1.46	0.387
10.0	1.84	0.512	10.0	1.71	0.407
20.0	2.32	0.594	20.0	1.90	0.380
40.0	2.77	0.567	30.0	1.99	0.306
70.0	3.12	0.513			

In Table V. K is the concentration in grams per liter, C the experimentally found conductivity and A_3 the constant of equation (16), calculated from the values of C and K. The variation of A_3 for Al_2Cl_6 is about 14 per cent. and for H_3BO_3 about 25 per cent.

In Figs. 12 and 13 the circled points represent values of conductivity calculated from equation (16), using the given values of K and average values of A_3. The agreement with the experimental curve is about as

good as could be expected, since it is not possible to measure these small conductivities with great accuracy.

A single measurement was made with uranium. The conductivity produced by a solution containing 10 grams of $UO_2(NO_3)_2$ per liter was found to be 3.19. When this solution was being sprayed the whole flame had a distinct sodium yellow color and a bright sodium line was seen when the flame was observed through a spectroscope. The flame also appeared to be filled with small luminous particles moving rapidly upward, giving it a streaked appearance. It is probable that the small conductivity observed was due to sodium impurity and that the $UO_2(NO_3)_2$ itself produced little or no conductivity.

In conclusion, I wish to express my sincere thanks to Professor H. A. Wilson for his valuable advice and kindly interest during the course of this work.

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A GENERALIZATION OF ELECTRODYNAMICS WITH APPLICATIONS TO THE STRUCTURE OF THE ELECTRON AND TO NON-RADIATING ORBITS.

BY LEIGH PAGE.

SYNOPSIS.

Generalization of Electrodynamics.—If every element of charge is assumed to be the center of equal electric and magnetic fields, each of which is capable of rotation, the electromagnetic equations assume a symmetrical form, containing Lorentz's formulation of Maxwell's equations as a special case.

Structure of the Electron.—If the electric field of each element of charge on the surface of the Lorentz electron is supposed to rotate about the normal to the surface, a magnetic field is produced which just annuls the intrinsic field due to the magnetic charge assumed to be distributed over the surface, and which exerts an inward stress equal to the outward stress of electrostatic repulsion. Not only is the surface in equilibrium, but the equilibrium is found to be stable for small volume changes.

Non-Radiating Electronic Orbits.—A suitable rotation of the fields of the elementary charges constituting the electron about an axis parallel to the acceleration would cause the radiation term to vanish. This suggests the possibility of radiationless orbits.

SEVEN years age the author of this paper proposed a kinematical interpretation of the electromagnetic equations[1] which both H. Bateman[2] and he[3] have since developed and generalized. In this interpretation electric charges are assumed to be the fundamental constituents of matter, magnetic poles existing only as secondary entities. Each element of electricity is supposed to emit uniformly in all directions with the velocity of light continuous streams of *moving elements*, or, as Bateman has termed them, *light particles*. Each moving element travels out from its source in a straight line uninfluenced by the subsequent motion of the source or by the presence or motion of neighboring moving elements. The nature of these moving elements is immaterial for the purposes of the theory other than that each must be susceptible of continuous identification and must move in a straight line with the velocity of light. A *line of electric force* is defined as the locus of a stream of moving elements emerging from a single source. To employ an analogy, a source may be likened to a machine gun firing bullets with the velocity of light. The bullets correspond to moving elements. If they are supposed to be

[1] Am. Jour. Sci., 38, p. 169, 1914.

[2] Phil. Mag., 41, p. 107, 1921.

[3] Proc. Nat. Acad. Sci., 6, p. 115, 1920.

strung along an endless perfectly elastic thread, such a thread constitutes a line of force. A charged particle, then, consists of a group of such guns pointing uniformly in all directions, each firing a continuous stream of bullets. If the charge is in motion, a line of force emerging from it will not in general have the same direction as the velocities of the moving elements which constitute the line. Thus arises a magnetic field, which has a direction at right angles to the electric lines of force and to the direction of motion of the moving elements constituting these lines, and an intensity proportional to the sine of the angle between these two vectors.

The number of lines of force emerging from an element of electric charge must be supposed to be very great. These lines may be grouped into bundles, each of which may be called a *tube of force*. The *electric intensity* $\mathbf{E}$ is defined as the number of tubes of force per unit cross section. If the light-velocity of the moving elements is denoted by the vector $\mathbf{c}$, the magnetic intensity $\mathbf{H}$ of an elementary field is defined by

$$\mathbf{H} = \frac{\mathbf{I}}{c} (\mathbf{c} \times \mathbf{E}).$$

The total electric or magnetic intensity at a point is the vector sum of the electric or magnetic intensities respectively of all the elementary fields which extend to that point.

Coulomb's and Ampère's laws follow at once as necessary consequences of this representation, and if the Lorentz-Einstein space and time transformations are used, Faraday's law and the law expressing the fact that the divergence of the magnetic intensity is zero, can be shown to hold exactly, provided the sources of moving elements do not rotate.[1] Thus the proposed representation contains the four field equations of electromagnetism. Furthermore, if it is assumed that the force on a charge e relative to an observer at rest with respect to the charge is given by the product $e\mathbf{E}$, the fifth equation of electrodynamics is easily deduced. In fact, the abundantly proven validity of this last relation, as interpreted on the basis of the representation under discussion, constitutes better experimental confirmation of the restricted relativity principle, perhaps, than any other evidence which has yet been adduced.

The generalization of the classical equations of electromagnetism which is obtained by taking into account the possibility of rotation of the sources of moving elements[2] is particularly suggestive. The field equations assume the symmetrical form (in Heaviside-Lorentz units)

[1] See L. Page, "An Introduction to Electrodynamics," Chap. II., Ginn & Co., 1921.

[2] Proc. Nat. Acad. Sci., 6, p. 120, 1920.

$$\nabla \cdot \mathbf{E} = \rho, \tag{1}$$

$$\nabla \times \mathbf{E} = -\frac{1}{c}(\dot{\mathbf{H}} + \epsilon \mathbf{u}), \tag{2}$$

$$\nabla \cdot \mathbf{H} = \epsilon, \tag{3}$$

$$\nabla \times \mathbf{H} = \frac{1}{c}(\dot{\mathbf{E}} + \rho \mathbf{v}), \tag{4}$$

where the velocity u of the free magnetism produced by a rotating field is in general equal to the velocity c of light. If the entire field rotates with the same angular velocity ω, then at a time r/c

$$\epsilon = \frac{e}{2\pi r^2 k^2 c^2} \frac{\omega \cdot \mathbf{c} - \omega \cdot \mathbf{v} k^2 \left(1 - \frac{\mathbf{c} \cdot \mathbf{v}}{c^2}\right)}{\left(1 - \frac{\mathbf{c} \cdot \mathbf{v}}{c^2}\right)^4}, \tag{5}$$

at a distance r from a charge e which is moving as a whole with velocity $\mathbf{v}$ at the time 0. The letter k stands for the reciprocal of $\sqrt{1 - \beta^2}$, β being the ratio of the velocity of the charge to that of light. If, now, the energy radiated for each complete rotation of the field is computed, it is found to have very closely the value

$$\frac{1}{32} h\nu,$$

where h is Planck's constant, and ν the frequency of rotation. This numerical coincidence suggests that quantum phenomena may be somehow connected with rotating electric fields.

The object of this paper is to propose a further generalization of the field equations, and to make applications to the structure of the electron and to non-radiating orbits.

Generalized Electrodynamics.

In the discussion immediately following, the terms *electric charge* and *magnetic charge* refer to an *element* of an electron or hydrion (positive electron), and not to charges so gross as even the entire charge on the electron. The postulates of the generalized theory are as follows:

1. With every electric charge is indissolubly associated an equal magnetic charge. By a charge is meant a center of uniformly diverging lines of force,—lines of electric force in the case of electric charges, and lines of magnetic force in the case of magnetic charges. Hence, from every element of the electron or hydrion radiate two sets of lines, one electric and the other magnetic. Since the Heaviside-Lorentz unit of charge is used in the following analysis, the magnitude e of the elementary charge is equal numerically both to the number of tubes of electric force and to the number of tubes of magnetic force radiating from it. The

electric intensity at any point is equal to the number of tubes of electric force per unit cross-section, and the magnetic intensity to the number of tubes of magnetic force per unit cross-section.

At first sight it may seem that this association of magnetism with electricity in the electron, for instance, is absurd in that it must give rise to a particle which has the properties of a magnetic pole as well as an electric charge. That such is not the case, however, will appear later on.

2. If $\mathbf{E}_1$ and $\mathbf{H}_1$ are the components of the electric and magnetic fields respectively at right angles to $\mathbf{c}$ due to an elementary charge e,

$$\mathbf{H}_1 = \frac{1}{c}(\mathbf{c} \times \mathbf{E}), \tag{6}$$

$$\mathbf{E}_1 = -\frac{1}{c}(\mathbf{c} \times \mathbf{H}), \tag{7}$$

just as in the classical theory. These are not independent relations, as either may be obtained from the other by forming the cross product with $\mathbf{c}$.

3. As in the classical theory, the force on an elementary charge e as measured by an observer relative to whom the charge is at rest at the instant considered, is

$$\mathbf{K} = e(\mathbf{E} + \mathbf{H}), \tag{8}$$

where $\mathbf{E}$ and $\mathbf{H}$ are the total field strengths. It follows from this that the force as measured by an observer relative to whom e is moving with velocity $\mathbf{v}$ is

$$\mathbf{K} = e\left(\mathbf{E} + \frac{1}{c}\mathbf{v} \times \mathbf{H} + \mathbf{H} - \frac{1}{c}\mathbf{v} \times \mathbf{E}\right), \tag{9}$$

the method of proof being the same as that used in obtaining the corresponding expressions in the paper[1] already referred to.

The expressions for the retarded electric and magnetic intensities due to an elementary charge e which has velocity $\mathbf{v}$ and acceleration $\mathbf{f}$ relative to the observer under consideration are obtained in the same manner as the corresponding expressions in the papers[1,3] referred to previously. They are

$$\mathbf{E} = \frac{e}{4\pi r^2 k^2 c\left(1 - \frac{\mathbf{c}\cdot\mathbf{v}}{c^2}\right)^3}\left\{\mathbf{c} - \mathbf{v} + \frac{1}{c}\mathbf{c} \times \mathbf{v} + \frac{rk^2}{c^3}\left[\left((\mathbf{f} - c\omega_H) \times (\mathbf{c} - \mathbf{v})\right\} \times \mathbf{c} + \left(\left\{\left(\omega_E + \frac{1}{c}\mathbf{f}\right) \times (\mathbf{c} - \mathbf{v})\right\} \times \mathbf{c}\right) \times \mathbf{c}\right]\right\}, \tag{10}$$

$$\mathbf{H} = \frac{e}{4\pi r^2 k^2 c\left(1 - \frac{\mathbf{c}\cdot\mathbf{v}}{c^2}\right)^3}\left\{\mathbf{c} - \mathbf{v} - \frac{1}{c}\mathbf{c} \times \mathbf{v} + \frac{rk^2}{c^3}\left[\left\{(\mathbf{f} + c\omega_E)\right.\right.\right.$$

$$\times (\mathbf{c} - \mathbf{v}) \Big\} \times \mathbf{c} + \left(\left\{ \left(\omega_H - \frac{\mathrm{I}}{c} \mathbf{f} \right) \times (\mathbf{c} - \mathbf{v}) \right\} \times \mathbf{c} \right) \times \mathbf{c} \Big] \Big\}, \quad (11)$$

where ω_E and ω_H refer to the electric and magnetic fields respectively. If ω_0 is the angular velocity of rotation of a field relative to an observer with respect to whom the charge producing the field is momentarily at rest, then the components of ω to be used in these equations by an observer relative to whom the charge has a velocity $\mathbf{v}$ in the x direction are related to the components of ω_0 by the following transformations,

$$\omega_x = \frac{\mathrm{I}}{k^3} \omega_{0x},$$

$$\omega_y = \frac{\mathrm{I}}{k^2} \omega_{0y},$$

$$\omega_z = \frac{\mathrm{I}}{k^2} \omega_{0z},$$

which are the same as the transformations of the components of acceleration.

It is observed that (10) and (11) satisfy conditions (6) and (7). Furthermore, *the radiation field vanishes* provided

$$\omega_E = -\frac{\mathrm{I}}{c} \mathbf{f}, \quad (12)$$

$$\omega_H = \frac{\mathrm{I}}{c} \mathbf{f}. \quad (13)$$

Therefore radiationless orbits are possible. It is to be noticed that the rotation of the field of an element of an electron does not in any manner imply rotation of the electron as a whole, and that the electric and magnetic fields may rotate at different rates and about different axes.

The field equations of the generalized theory are the equations (1) to (4) already given. The divergence ρ of the electric vector may conveniently be split into two parts, the density ρ_0 of electric charge and the divergence ρ_H due to rotation of the magnetic lines of force. Similarly ϵ consists of the density of magnetic charge ϵ_0 and the divergence ϵ_E of the magnetic vector due to rotation of the electric lines of force. According to postulate (1) $\rho_0 = \epsilon_0$ always. The retarded expressions for ρ_H and ϵ_E due to a charge e moving with velocity $\mathbf{v}$, whose electric field has angular velocity ω_E and magnetic field angular velocity ω_H, are respectively

$$\rho_H = -\frac{e}{2\pi r^2 k^2 c^2} \frac{\omega_H \cdot \mathbf{c} - \omega_H \cdot \mathbf{v} k^2 \left(\mathrm{I} - \frac{\mathbf{c} \cdot \mathbf{v}}{c^2} \right)}{\left(\mathrm{I} - \frac{\mathbf{c} \cdot \mathbf{v}}{c^2} \right)^4}, \quad (14)$$

$$\epsilon_E = \frac{e}{2\pi r^2 k^2 c^2} \frac{\omega_E \cdot \mathbf{c} - \omega_E \cdot \mathbf{v} k^2 \left(1 - \frac{\mathbf{c} \cdot \mathbf{v}}{c^2}\right)}{\left(1 - \frac{\mathbf{c} \cdot \mathbf{v}}{c^2}\right)^4}. \quad (15)$$

It should be noticed that while ρ_H and ϵ_E are divergences in the electric and magnetic vectors respectively, they are due to the rotations of the lines of force and are not to be considered as true charges. A charge is detected by its field, and the divergences under discussion lack the characteristic uniformly diverging field of a charge. They are merely the end points of broken off lines of force which originate on a charge.

The energy equation is obtained by the usual methods from the field equations (1) to (4). It is

$$\frac{d}{dt}\{\tfrac{1}{2}(E^2 + H^2)\} + c\nabla \cdot (\mathbf{E} \times \mathbf{H}) + \mathbf{E} \cdot \mathbf{v}\rho + \mathbf{H} \cdot \mathbf{u}\epsilon = 0. \quad (16)$$

The last two terms represent the rate at which work is done on the divergences of $\mathbf{E}$ and $\mathbf{H}$, whether these divergences are true charges or end points of broken off lines of force;

$$\tfrac{1}{2}(E^2 + H^2)$$

is the field energy per unit volume; and

$$(c\mathbf{E} \times \mathbf{H})$$

the Poynting flux.

STRUCTURE OF THE ELECTRON.

The Lorentz electron is the simplest model which has yet been proposed. This electron is a uniformly chargek spherical shell relative to an observer with respect to whom it is at rest at the instant considered. It may easily be shown that all points of the electron are at rest relative to a given observer at the same time. If the electron is in motion, the relativity contraction causes it to appear shorter in the direction of motion than if it were at rest. Its dimensions at right angles to the direction of motion are unaltered. Each element of charge of the electron is assumed to act on every other element according to the same law of force as governs the actions of gross charges on one another. Hence the repulsive force expressed by Coulomb's law produces an outward stress at the surface of the electron which would cause it to explode in the absence of some inward force not explicable in terms of the classical electrodynamics. This outward stress is the same for an electron moving with constant velocity as for one at rest, and normal to the surface in both cases. Hence Poincaré has been led to suggest that it is counterbalanced by a uniform hydrostatic pressure of the ether. This hypothesis is open to several objections. In the first place, it requires the existence of

forces of a character quite different from those contained in the electromagnetic scheme, as well as a second type of interaction between ether and electricity. Secondly, it implies the absence of ether from the interior of the electron, which is inconsistent with the assumption that electromagnetic forces are propagated across the inside of the electron from one element of charge to another. Thirdly, it is at variance with evidence showing that the ether (if one may be allowed to use the term) cannot have many, if any, of the properties of material media.

When an electron is moving with any other type of motion than constant velocity, its field exerts a drag on it. This retarding force is proportional, to a first approximation, to the acceleration, and accounts for the mass of the electron. The mass formula involves the radius of the electron, its charge, and the velocity of light. The last two being known, the first may be calculated, and comes out to be $1.88(10)^{-13}$ cm., which is of the order of magnitude to be expected. If the electron is assumed to have a volume distribution of charge expressible by any arbitrary function of the distance from its center, instead of the surface distribution of the Lorentz model, the value of the radius comes out somewhat different, though of the same order of magnitude, and the ether, if Poincaré's hypothesis be accepted, must be supposed to penetrate into the interior with a density which falls off as the center is approached. However, the objections to this hypothesis cited above still hold. The object of this section of the present paper is to show that the proposed generalized electrodynamics makes it possible to account for both the equilibrium and the stability of the electron without the necessity of introducing extra-electromagnetic forces.

Lorentz's model will be adopted in that the electron will be supposed to be a uniformly charged spherical shell of charge e and radius a. Each element of charge is the origin of equal electric and magnetic fields. The magnetic fields will be supposed, normally, to be without rotation; the electric field of each element of charge, on the other hand, will be considered to have a constant angular velocity ω about the normal to the surface at the point considered. Consider, now, an electron permanently at rest relative to the observer. Expressions (10) and (11) for the electric and magnetic intensities respectively due to an element de of the electron's charge reduce to

$$d\mathbf{E} = \frac{de}{4\pi r^2 c}\left\{ \mathbf{c} - \frac{r}{c}\,\boldsymbol{\omega} \times \mathbf{c} \right\}, \tag{17}$$

$$d\mathbf{H} = \frac{de}{4\pi r^2 c}\left\{ \mathbf{c} + \frac{r}{c}\left[\frac{\boldsymbol{\omega} \cdot \mathbf{c}}{c^2}\,\mathbf{c} - \boldsymbol{\omega} \right] \right\}. \tag{18}$$

Symmetry shows that the resultant **E** and the resultant **H** are radial. Integrating over the surface of the electron, the intensities at a point P (Fig. 1) outside the electron and distant p from its center are found to be

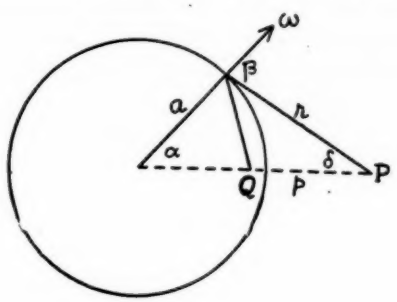

Fig. 1.

$$E = \frac{1}{4\pi}\int \frac{\cos\delta}{r^2}\,de$$
$$= \frac{e}{16\pi a p^2}\int_{p-a}^{p+a}\left[1 + \frac{p^2 - a^2}{r^2}\right]dr$$
$$= \frac{e}{4\pi p^2}, \tag{19}$$

$$\mathbf{H} = \frac{1}{4\pi}\int\left[\frac{\cos\delta}{r^2} + \frac{\omega}{cr}(\cos\beta\cos\delta - \cos\alpha)\right]de$$
$$= \frac{e}{16\pi a p^2}\int_{p-a}^{p+a}\left[1 + \frac{p^2 - a^2}{r^2}\right]dr$$
$$+ \frac{e\omega}{32\pi a^2 p^2 c}\int_{p-a}^{p+a}\left[r^2 - 2(p^2 + a^2) + \frac{(p^2 - a^2)^2}{r^2}\right]dr$$
$$= \frac{e}{4\pi p^2}\left[1 - \frac{2}{3}\frac{a}{c}\omega\right]. \tag{20}$$

Choose

$$\omega = \frac{3}{2}\frac{c}{a}$$
$$= 2.40\ (10)^{23}\ \text{per sec.} \tag{21}$$

Then there is no magnetic field outside the electron, and the electric field follows Coulomb's familiar inverse square law.

At a point Q inside the electron, the same integral expressions for E and H hold, but the limits of integration are $a + p$ and $a - p$ instead of $p + a$ and $p - a$. Hence

$$E = 0, \tag{22}$$
$$H = -\frac{e\omega p}{6\pi a^2 c}$$
$$= -\frac{ep}{4\pi a^3}, \tag{23}$$

The electric field vanishes, and the magnetic field is directed toward the center and has a strength proportional to the distance p from the center.

The divergence of the electric vector is everywhere zero (except at the surface). The divergence of the magnetic vector is zero outside the surface, but (23) shows that inside it must have the constant value

$$\nabla \cdot \mathbf{H} = -\frac{e\omega}{2\pi a^2 c} = -\frac{3e}{4\pi a^3}. \tag{24}$$

Thus the total volume distribution of divergence of the magnetic vector inside the electron is equal and opposite in sign to the surface magnetic charge, agreeing with the computed absence of magnetic field outside the electron. The divergences of $\mathbf{E}$ and $\mathbf{H}$ might have been obtained directly from (14) and (15).

At the surface of the electron, E and H have the same values but opposite directions. Hence the charge on the surface is in equilibrium. The outward stress due to the electric field is

$$S = \frac{e^2}{32\pi^2 a^4}, \tag{25}$$

per unit area, and the equal inward stress due to the magnetic field

$$S = \frac{e^2\omega^2}{72\pi^2 a^2 c^2}. \tag{26}$$

Let the radius of the electron increase to $a + x$, the angular velocity ω retaining the value given above. Then the net outward stress is

$$S = \frac{e^2}{32\pi^2 a^4}\left[-2\frac{x}{a} + 7\frac{x^2}{a^2}\cdots\right]. \tag{27}$$

The electron, therefore, is in stable equilibrium as regards changes in volume.

The generalized electrodynamics under discussion has been derived directly from the relativity principle, and hence all deductions to which it leads must be strictly in accord with this principle. Therefore the conclusions arrived at regarding equilibrium and stability of an electron permanently at rest apply equally well to an electron moving with constant velocity relative to the observer. In the latter case a magnetic field external to the electron is present, but it is the ordinary field due to motion of the electron as a whole, and not due to the rotations of the generalized theory. The divergences of both vectors are zero everywhere outside the electron.

These speculations as to the nature of the electron suggest that the positive electron or hydrion differs from the negative electron in the sense of the rotation ω. If, for instance, the rotation of the field of an element of charge on the surface of the negative electron is clockwise when viewed along the outward drawn normal, the rotation may be counterclockwise in the case of the positive electron. The fact that only two senses of rotation are possible is in accord with the existence of two and only two kinds of electricity.

Non-Radiating Orbits.

Integration over the entire surface of an unaccelerated electron has shown that **E** and **H** have the same values outside the surface as are predicted by Maxwell's classical equations. The rotations of the electric fields of the elements of charge constituting the electron annul one another in such a manner as to produce no resultant effect in so far as the electric intensity is concerned. An investigation of the external field and the dynamical equation of an accelerated electron is being undertaken in the hope that it may throw some light on quantum phenomena. For the results of Rutherford's experiments on the scattering of alpha rays are very excellent evidence, in the author's opinions that quantum phenomena cannot be accounted for by substituting for the inverse square electrostatic field of the nucleus amore complicatedfield involving repulsive as well as attractivef orces. Hence it would seem as though the quantum must be somehow or other connected with the electron.

The conditions for annulment of the radiation field have been already stated. The necessary small angular velocities in the direction of the acceleration must be supposed to be superimposed on the much larger angular velocity of the electric fields normal to the surface. In the case of an electron rotating in a circular orbit of quantum number n about a nucleus of atomic number Z,

$$\begin{aligned} \omega_H &= -\omega_E = \frac{\mathrm{I}}{c}\mathrm{f} \\ &= \frac{16\pi^4 me^6}{h^4 c}\frac{Z^3}{n^4} \\ &= 3.01\ (10)^{14}\frac{Z^3}{n^4}\text{ per sec.}, \end{aligned} \tag{28}$$

which is quite negligible compared to (21).

Note Added in Course of Publication.—Further calculation shows that the mass and the cofficient of the rate ot change of acceleration are each one and a half times as great as for the simple Lorentz electron of the

same radius. Hence, the mass being known, the radius of the proposed electron comes out one and a half times as great as that of the Lorentz type, i. e., $2.82(10)^{-13}$ cm.

While the suggested superimposed rotations of the electric and magnetic fields of a revolving electron annul the radiation due to acceleration of the electron as a whole, there remains a radiation of the same order of magnitude due to the rotation about the normal to the electron's surface of the electric fields of each element of charge. If the superimposed rotations are such as to annul *entirely* the radiation field of each element of charge, the equilibrium of the electron's surface is interfered with, and the electromagnetic mass of the electron vanishes.

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AN ELECTRICAL DOUBLET THEORY OF THE NATURE OF THE MOLECULAR FORCES OF CHEMICAL AND PHYSICAL INTERACTION.

By R. D. Kleeman.

Synopsis.

Electrical doublet theory of molecular attraction.—The author has previously found from data on the internal heat of evaporation of liquids that the attraction between two atoms is proportional to the product of the square roots of their atomic weights. It is now suggested that a neutral atom with a positive nucleus surrounded by electrons is an electrical doublet; and it is shown that the force between two such doublets would on the average be an attraction proportional to the product of the moments of the two doublets. This result combined with the previous one leads to the conclusion that the *electrical moment of an atom* is proportional to the square root of its atomic weight. Similarly the electrical moment of a molecule comes out equal to the sum of the moments of the component atoms. This theory of molecular attraction is supported by the fact that the *stopping power of gases for alpha rays* is known to be proportional to the sum of the square roots of the atomic weights of the component atoms; for this law follows directly if we suppose the transfer of energy from the alpha particles to the gas molecules occurs solely as a result of electrical forces exerted by the charged rays on the molecular doublets.

Previous Investigations of the Molecular Forces

It will be instructive and useful to consider as an introduction to the subject of this paper the nature of the law of force between two molecules which can be deduced directly from physical data. I have shown[1] that the force of attraction between two molecules deduced from data on the internal heat of evaporation of liquids, is given by the expression

$$\frac{\phi\left(\frac{T}{T_c}, \frac{z}{x_c}\right)}{z^5} \cdot (\Sigma \sqrt{a})^2,$$

where z denotes the distance of separation of the two molecules in the liquid whose temperature is T, x_c the average distance of separation of molecules of the liquid at the critical point whose critical temperature is T_c, $\Sigma \sqrt{a}$ denotes the sum of the square roots of the atoms of a molecule, and $\phi(T/T_c, z/x_c)$ is a function whose form is left arbitrary by the data, and which for shortness will be denoted by (ϕ). It appears from the foregoing expression that the attraction between two molecules is a

[1] Phil. Magazine, May, 1910, pp. 783–809; Jan., 1911, pp. 83–102. Proc. Camb. Phil. Soc., XVI., Pt. 7, pp. 583–598.

function of their temperature as well as of their distance of separation. We would expect, of course, that the attraction between two molecules might depend on the temperature, since a change in temperature is accompanied by a change in the internal molecular energy, which probably involves a change in atomic configuration, as is shown by the positive value of the specific heat. The foregoing law, it should be remarked, was obtained from latent heat data taking into account the following mathematical theorem: The nature of a function F of two independent variables x and y can be determined approximately in a definite manner only from data giving the values of the function corresponding to variations of each of the variables keeping the other constant, while if the form of the function is determined from data corresponding to the simultaneous variation of x and y it will contain an arbitrary function. A corollary of this theorem is, if the assumption is made that the function contains one variable only, and a form of the function is found agreeing with the facts, this does not signify that the assumption made is true. Now the density of a liquid changes on change of temperature, and the internal heat of evaporation is therefore a function of the two independent variables temperature and distance of separation of the molecules, which vary simultaneously. The law deduced from such data by itself should therefore contain an arbitrary function, and the nature of this function must accordingly be determined by considering in addition data relating to other quantities. This has been carried out by the writer[1] but the results need not concern us here, except that the function varies little with z and T. For our present purpose it is important to notice that the function involves quantities depending on the critical state of the substance to which it refers, which indicates that the nature and magnitude of the attraction between two molecules in the substance is influenced by the surrounding molecules, as we might expect.

THE MOLECULAR FORCES ARE EXPLAINED BY CONSIDERING THE ATOMS AS ELECTRICAL DOUBLETS.

In this paper an attempt will be made to explain the nature of the molecular attraction under consideration (which give rise to the internal heat of evaporization of a liquid, its surface tension, intrinsic pressure, chemical interaction between its atoms and molecules, etc.) by the electric charges each atom is supposed to contain. It will be of interest and serve as an introduction to the main investigation, to consider the attraction which one of the electrical charges in an atom would exert on another atom, supposing that the latter atom behaves as a spherical

[1] *Loc. cit.*

conductor of electricity. The attraction in that case is given by the well known expression

$$\frac{e^2 r_1^3 (2f^2 - r_1^2)}{f^3 (f^2 - r_1^2)^2},$$

where e denote the electric charge in the former atom, r_1 the radius of the latter atom, and f the distance between their centers. When r_1^2 is small in comparison with f^2 this expression reduces to

$$\frac{2e^2 r_1^3}{f^5}.$$

Now we have seen that the function ϕ in the law of molecular attraction does not vary much with z and T, in which case the attraction between two molecules varies approximately inversely as the fifth power of their distance of separation, and thus corresponds to the foregoing expression. But the resemblance goes further. Traube has shown[1] that the apparent volume of an atom at the absolute zero is approximately proportional to the square root of its atomic weight, and hence r_1^3 is proportional to $\sqrt{a}$. Therefore if we make the assumption that the total electric charge of one sign associated with an atom is proportional to $\sqrt{a}$ (this is roughly the case) we obtain that the electric attraction between two atoms c and e is equal to

$$\frac{k \sqrt{a_c} \sqrt{a_e}}{f^5},$$

where a_c and a_e denote the atomic weights of the atoms, and k a constant. The attraction between two molecules of the same kind composed of various atoms would accordingly be given by

$$\frac{k(\Sigma \sqrt{a})^2}{f^5}.$$

This expression contains the fundamental factor $\Sigma \sqrt{a}$ contained in the law of attraction deduced from latent heat data.

The atom must however more properly be regarded in all cases as an assemblage of electrons and positive charges instead of a spherical conductor of electricity, whose effect on an external electron, or on another atom, is more or less equal to the total sum of the effect of each electrical charge. Now according to Rutherford[2] the atom consists of a number of electrons located near the surface of the atom, and a corresponding positive charge concentrated more or less at the center. It is very probable that the electrons and corresponding positive charges of an atom are not arranged in a symetrical way with respect to the center of the atom. Under these conditions the atom would as a whole behave

[1] Physik. Zeit., Oct., 1909, p. 667.

[2] Phil. Mag., 21, p. 669, 1911.

approximately like an electrical doublet. Now it can be shown that the orientation of the axes of the atomic doublets would on the average be such as to produce attraction between the atoms. Thus suppose that the atoms are stationary in space and occupy their average positions, which correspond to the points of intersection of three sets of equidistant planes situated at right angles to each other. Suppose that the axes of the electrical doublets of a row of atoms lie on the straight line joining them, and that the charges are so arranged that opposite kinds face one another. Under these conditions the atoms will attract each other, tending to move along the straight line joining them. Let us also suppose that the atoms in an adjacent parallel row be similarly arranged except that the positive charge of each doublet faces in the opposite direction with respect to the negative charge, as shown in Fig. 1. It will be evident that we may suppose that the set of atoms consists of parallel rows of the foregoing kind lying in parallel planes, and that in each alternate row of the rows lying in a plane the positive charges face one way, and in the other rows face in the opposite way. Hence we may also look upon the atoms as being divided up into a number of parallel rows at right angles to the foregoing rows, in which the charges of opposite sign will be nearer to each other than the charges of the same kind. Thus the atoms would also exert an attraction upon each other along the directions of these rows. Hence the atoms would exert an attraction upon each other in all directions, tending to contract the set of atoms as a whole.

Fig. 1.

In practice however, the atoms or molecules, are not stationary in space, but undergo motion of translation, which gives rise to collisions with each other, which have the effect of abruptly changing the orientations, or the directions of rotation, of the axes of the electrical doublets. But according to the principle that *the potential energy of a system tends to become a minimum*, the axes of the doublets would tend to point on the average in such directions as will give rise to an attraction between the atoms. A closer examination will show how this may be brought about. The axis of a doublet points successively in different directions in space through molecular collisions. Each direction will occur equally frequently since the substance as a whole has no electric polarity. But the successive directions of one atomic doublet are connected with the successive directions of an adjacent atomic doublet. For the axes of the doublets would tend to point parallel to each other, through the

forces of attraction and repulsion which the charges of the doublets exert upon each other. Hence the axis of an atomic doublet would be oftener parallel to that of another atomic doublet than at right angles to it. This would give rise to attraction tending to be the outstanding force between the doublets. The extreme case of such a connection between the positions of the atomic doublets with respect to each other would be if the atomic doublets in Fig. 1 were to rotate round their centers in any manner but with their axes remaining parallel to each other.

It may happen, of course, that for certain densities of the substance the effect of molecular collision on the orientation of the axes of the electrical doublets may be such that repulsion is produced between the atoms instead of attraction. According to the foregoing principle connected with potential energy this repulsion would tend to be as small as possible. Thus atomic repulsion, whose existence is shown by the Joule Thomson effect, may be explained as well as attraction by the existence of electrical doublets.

In the case of two molecules the forces of attraction and repulsion would be due to the effect of the atomic doublets of one molecule on those of the other. The effect of each atomic doublet on another doublet would very probably be independent of the presence of the other doublets, and the electrical effect of a molecule would therefore in a sense be an additive quantity of its atoms.

It will be of interest next to examine the algebraical nature of the law of force according to the foregoing supposition. It can be easily shown that the force between two electrical doublets of magnitude M' and M'' is

$$\frac{M'M''}{r^4} 3\{2 \cos\cdot\theta\cdot\cos\theta' - \sin\theta\cdot\sin\theta'\} = \frac{M'M''}{r^4} C_e,$$

where r denotes the distance between the centers of the doublets and θ and θ' the angles the doublets make with the line joining their centers. In the case in which the doublets belong to two atoms of a mon-atomic substance in the liquid or gaseous state the quantity C_e would be a function of the two average angles the doublets make with the line joining them. These angles would evidently depend on the frequency of atomic collision in the substance, and on the nature of a collision, and hence would depend on the temperature and density of the substance, and on its nature, *i.e.*, on its temperature, distance of atomic separation, atomic weight, and critical constants. In the case that the substance consists of molecules, M' would consist of the sum $(M_1' + M_2' + \cdots)$ of the atomic doublets of a molecule, and M'' of the sum $(M_1'' + M_2'' + \cdots)$

of the doublets of another molecule. When repulsion exists, as we have seen may be the case, the sign of C_e is negative.

The foregoing results are borne out by experiment. According to what has gone before the quantity C_e would be proportional to

$$\frac{1}{z}\cdot\phi\left(\frac{T}{T},\frac{z}{x_e}\right),$$

and thus a function of the temperature of the substance, the distance of molecular separation, and the critical constants. It appears also that the moment of each electrical doublet is proportional to $\Sigma\sqrt{a}$, the sum of the square roots of the atomic weights of the atoms. This result will be confirmed by other evidence later.

It will be of interest next to consider more closely the distribution of the electrons and positive charges in an atom. According to the experiments of Rutherford mentioned the positive charge is concentrated in a sphere of radius less than 10^{-12} cm. From considerations of symmetry we would expect this charge to be the electrical center of the atom. Since the number of electrons is finite it is evident that they cannot be arranged around the positive charge in such a way that the electric force is zero on any point on a line passing through the positive charge. If the point selected is at a distance from the positive charge which is large in comparison with the distance of each electron, the effect is approximately equivalent to the sum of the effects of a number of doublets each of which corresponds to an electron in the atom, *i.e.*, the atom as a whole behaves approximately like an electrical doublet. This corresponds to the state of affairs in practice, where the forces we are dealing with correspond to an average distance of separation of the atoms or molecules which is much larger than the atomic and molecular diameters. Of course, on rotating an atom round its center the moment of the average doublet will change somewhat, and we must therefore associate an average doublet with an atom which includes the consideration of direction from the atomic center. It is, of course, also not improbable that the positive charge is not located at the center of the atom.

If the two electrical charges of the representative doublet of an atom were separated by the same distance in all cases, each charge would be proportional to the square root of the atomic weight. But this is not likely to be the case. Moreover there is good reason to believe from various evidence that the number of unit positive charges in an atom is equal to A its atomic number. Therefore if x denote the distance of separation of the charges of the representative doublet of an atom, we have

$$xA = \sqrt{a}.$$

Now the atomic number increases with the atomic weight, and for high atomic weights is approximately half of the atomic weight. Thus it appears that the distance x decreases with the atomic weight of the atom. This is probably due to the fact that the larger the number of electrons in an atom, the nearer can their distribution be made symmetrical around the positive charge.

Since the nature of the quantity C_e in the expression for the force of two atomic or molecular doublets upon each other, which corresponds to the function (ϕ) in the law of molecular attraction, depends on the average orientation of the atomic or molecular doublets with respect to each other in a substance, the function (ϕ) would depend, as has already been pointed out, on the nature of the atomic and molecular interaction. It should therefore be a function of the temperature and the density of the substance, as we have already seen is the case. In general, it will be evident that any process that will change the nature of the molecular interaction will change the nature of the function (ϕ).

Thus for example, in the case of a mixture of molecules a and c the nature of the interaction of a molecule a, or c, with other molecules would be different from that when the constituents are in the pure state. The attraction between two molecules a would then be given by the general expression

$$\psi(R_a', \rho) \cdot (\Sigma \sqrt{a})^2,$$

where R_a' denotes the ratio of the different constituents of the mixture, and ρ its density. The nature of the function ψ could evidently not be predicted from the form of (ϕ) applying to a pure substance. Similar remarks apply to the nature of the force between two molecules a and c, or two molecules c. The nature of the function ψ could be determined only from data relating to mixtures.

The nature of the molecular interaction of the molecules of a liquid would evidently be changed by the application of an electric field, since it would tend to set the doublets parallel to each other, and a corresponding change in the law of molecular attraction would be introduced. This might therefore be attended by a change in the volume of the substance. Since molecules and atoms possess magnetic properties a magnetic field would act in the same way.

The motion of a substance through space would tend to make the electrical atomic doublets set themselves with their axes at right angles to the motion, an effect which would become very marked when the velocity of the substance approaches that of light. This would obviously change the nature of molecular interaction, and accordingly a change in the functional nature of the law of molecular attraction be introduced.

Hence on giving a motion to a liquid it would undergo a contraction or an expansion as the case may be. When the substance is a solid the change in length in the direction of the motion might be different from that at right angles to it.

Since light consists of electromagnetic waves, or of waves of electric and magnetic force, it would have the effect of changing the nature of molecular interaction to a certain extent and hence the nature of the forces of interaction. The chemical changes induced by light in liquids and gases could be well and strikingly explained in this way.

THE PASSAGE OF THE α PARTICLE THROUGH MATTER.

The behavior of a charged particle passing through matter is intimately connected with the foregoing considerations. Bragg and the writer[1] have carried out some measurements on the range of the α particle in different gases, that is, the distance it traverses during which its energy decreases to a certain fraction of its original value. The α particle, it should be mentioned, is according to Rutherford a helium atom carrying a positive charge equal to $2e$. It was found that the range is inversely proportional to the sum of the square roots of the atomic weights of the atoms of a molecule of the gas. The passage of an electron through matter (the electron carries a negative charge equal to e), one would expect, should be subject to the same law. The writer has obtained some evidence that this is the case for velocities of the electron of the same order as those of the α particle.[2]

Let us suppose that the α particle mainly spends its kinetic energy in increasing that of the molecules along its path by means of the forces of attraction and repulsion it exerts upon them. Now Maxwell has investigated the motion of a molecule that expends its energy in a gas in this way for the case when the molecule is attracted or repelled by a molecule of the gas according to a law of the form K/z^n, where z denotes the distance of separation of the interacting molecules, and K and n are constants.[3] Thus the decrease of the velocity V of a molecule of mass m_2 in passing over a distance dx in a gas whose molecules are each of mass m_3, is according to this investigation given by

$$\frac{dV}{dx} = \frac{-m_3}{m_2 + m_3}\left(\frac{K(m_2 + m_3)}{m_2 m_3}\right)^{2/(n-1)} NA_c V^{(n-5)/(n-1)},$$

where N denotes the number of molecules in the gas per cubic cm., and A_c a constant which is independent of m_2, m_3 and V. The force between

[1] Phil. Mag., 10, 1905, p. 318.

[2] Proc. Roy. Soc., A, vol. 84, p. 20, 1910.

[3] Conduction of Electricity through Gases, by J. J. Thomson, 2d ed., p. 371.

a neutral gas molecule and a charged α particle, according to the preceding Article, corresponds to the force between the electrical doublet of the neutral molecule, and the electrical charge and the electrical doublet of the α particle. It will not be difficult to see that the force between the two doublets is small in comparison with that due to the doublet of the neutral molecule and the charge on the α particle, and hence the latter force only need be considered. It can easily be shown that if a charged particle is situated on the prolongation of the axis of a doublet the force between the two is $M2e/r^3$, where M denotes the moment of the doublet, $2e$ the charge on the particle, and r their distance of separation. This force may be either positive or negative in sign as the case may be. The doublet of a molecule is however continually undergoing varying oscillations and rotations. The average force between a neutral molecule and the α particle during its motion through the gas, may thus be written $C_e' \cdot M/r^3$, where C_e' is a constant. It might be conjectured at first sight that C_e' is a function of the temperature and density of the gas. But this is evidently not the case since the various positions of the doublets of the neutral molecules *with respect to the rapidly passing α particle* must be symmetrically distributed in space because the gas as a whole has no polarity, and hence these positions are independent of the concentration and temperature of the molecules. The moment M of the doublet of a molecule is according to the preceding Article proportional to the sum of the square roots of the atoms of a molecule, or proportional to $\Sigma \sqrt{a}$. The law of force between the α particle and a neutral molecule may accordingly be written $C_x \Sigma \sqrt{a}/z^3$, where C_x is a constant. The above equation then reduces to

$$\frac{dV}{dx} = \frac{C_x}{m_2} \Sigma \sqrt{a} \cdot \frac{NA_e}{V},$$

which on multiplying by $m_2 V \cdot dx$ and integrating becomes

$$m_2(V_1^2 - V_2^2) = C_x(x_1 - x_2)\Sigma \sqrt{a}.$$

This equation states that an α particle whose energy falls from $\frac{1}{2}m_2V_1^2$ to $\frac{1}{2}m_2V_2^2$ traverses a distance $x_1 - x_2$, which is inversely proportional to the square roots of the atomic weights of the atoms of a molecule of the gas. This is the law found by experiment, and which is thus in a striking way explained by the existence of electrical doublets in atoms and molecules.

It is interesting to note that according to the foregoing investigation the rate at which an α particle spends energy on a molecule is independent of the density and temperature of the gas through which the α particle

passes. This is borne out by the experimental results. It also follows from the investigation that the α particle will cease spending its energy in the way deduced when it has lost its charge.

In the foregoing investigation it was assumed that the α particle spends its energy mainly in interacting with neutral molecules. This will appear highly probable when it is considered that less than ten molecules of ten thousand molecules lying in the path of the α particle are likely to get ionized.

PHYSICAL LABORATORY,
UNION COLLEGE,
SCHENECTADY, N. Y., March 23, 1921.

PROCEEDINGS

OF THE

AMERICAN PHYSICAL SOCIETY.

MINUTES OF THE BERKELEY MEETING, AUGUST 4, 1921.

THE 110th meeting of the American Physical Society was held in Room 113, South Hall, University of California, Berkeley, on Thursday, August 4, 1921. Professor W. B. Anderson presided. About 75 persons were in attendance. At the morning and afternoon sessions, beginning at 9:30 and 2 o'clock respectively, the following program was presented:

The Moon's Electric Charge. FERNANDO SANFORD.

Earth Currents and the Sun's Electrical Induction. FERNANDO SANFORD.

The Effect of Temperature on the 3883 Cyanogen Band. RAYMOND T. BIRGE.

Some X-Ray Isochromats. D. L. WEBSTER.

The Width of X-Ray Spectrum Lines. ARTHUR H. COMPTON.

The Effect of Damping on the Width of X-Ray Spectrum Lines. G. E. M. JAUNCEY.

Experiments on Polarization of X-Rays. PAUL KIRKPATRICK.

An X-Ray Spectrometer for the Determination of Absorption Coefficients. ELMER DERSHEM.

A Photographic Method of X-Ray Crystal Analysis. ELMER DERSHEM.

Secret Photoelectric Signaling. ELMER DERSHEM.

An Harmonic Curve Writer. WILLIAM J. RAYMOND.

The Variation of the Thermal Conductivity of Iron with Temperature. E. F. HALL, O. R. HULL, and O. S. IMHOFF.

The Index of Refraction of Water, Ethyl Alcohol, and Carbon Bisulphide at Various Temperatures. A. R. PAYNE and E. E. HALL.

Preliminary Report on Spectroscopic Investigations in the Extreme Ultra-Violet. J. J. HOPFIELD.

The Effect of Pressure on the Band Spectrum of Nitrogen. JEAN HUDDLESTON.

The Reaction of Iron with Nitric Acid. JOSEPH G. BROWN.

A Braun-Tube, Undamped-Wave, Precision Method of Determining Dielectric Constants of Gases. L. T. JONES and H. G. TASKER.

The Effect of Ultra-Violet Light on the Viscosity of Rubber Colloids. RICHARD HAMER.

The Simplest Mercury Vapor Pump. L. T. JONES.

A New Rotary Mercury Pump. L. T. JONES.

Atomic Radii. MAURICE L. HUGGINS.

Structure of the L-Series of Tungsten and Platinum. FRANK C. HOYT.

The Sun's Charge. A Criticism of Method. F. J. ROGERS.

Preliminary Determination of the Critical Potentials of the M Lines in the Lead X-Ray Spectrum. P. A. ROSS.

Recent Observations of Absorption Spectra. A. S. KING. (Read by title.)

A Possible Origin of the Defect of the Combination Principle in X-Rays. ARTHUR H. COMPTON.

At the conclusion of the meeting the audience listened to a concert at the Fairmount Hotel, San Francisco, transmitted by wireless telephone, arranged by Mr. H. G. Tasher.

E. P. LEWIS,
Local Secretary for the Pacific Coast.

THE MOON'S ELECTRIC CHARGE.

BY FERNANDO SANFORD.

AT the January, 1921, meeting of this society I reported some observations on the diurnal change in electric potential-difference between the earth and an uncharged, insulated conductor kept inside an earthed metal cage. These variations were attributed to the electrostatic induction of the sun's negative charge. Photographic records of these variations have now been kept for a year.

In the meantime the diurnal variations due to the moon have been computed for five lunation periods of 29 days each. Three of these sets were made by distributing the data derived from the measurements of the photographic records for each hour of the solar day with reference to the position of the moon. Thus, the measurement made nearest the time of the moon's upper culmination was taken as the middle of the lunar day, and the twelve hourly measurements preceding and the twelve following this one were distributed in their proper order with reference to it.

Two of the sets were made by Chapman's method of subtracting the mean of the measurements for a given hour for the whole period from each of the single measurements made at that hour of the day, and distributing the residuals, either positive or negative, to the proper hour of the lunar day, just as the total measurements at the given hours were distributed in the previous cases. This method seems to possess no advantages over the other in determining the moon's electrostatic effect.

The data derived from the five series are given in Table I.

It will be seen from Table I. that while the diurnal variation is plainly shown in all the series the maximum positive variation came much later in Series 5 than in any of the others. No reason for this is known. The maximum positive solar variation for the same period came at noon.

TABLE I.

Mean Diurnal Variation in Potential-Difference, Expressed in Millivolts, between the Earth and an Uncharged, Insulated Conductor Due to the Moon's Electrostatic Induction.

Hour.	Series 1.	Series 2.	Series 3.	Series 4.	Series 5.	Mean of 5.
1	+ 0.5	− 4.7	− 0.6	− 5.3	− 3.6	− 2.7
2	− 0.3	− 5.2	− 0.7	− 7.3	− 4.2	− 3.5
3	− 1.7	− 5.3	+ 0.2	− 7.0	− 3.6	− 3.5
4	− 1.6	− 4.7	+ 0.8	− 7.1	− 5.5	− 3.6
5	+ 0.9	− 1.1	− 2.2	− 4.6	− 3.6	− 2.1
6	+ 1.6	+ 0.5	− 2.4	− 3.7	− 1.0	− 1.0
7	+ 3.3	+ 2.8	− 2.5	+ 0.4	− 1.1	+ 0.6
8	+ 4.6	+ 4.3	+ 0.6	− 0.4	− 0.5	+ 1.7
9	+ 5.4	+ 5.6	− 0.5	+ 4.5	− 1.1	+ 2.8
10	+ 5.2	+ 6.7	+ 2.9	+ 7.9	− 3.0	+ 3.9
11	+ 4.1	+ 6.8	+ 2.0	+ 7.6	− 6.5	+ 2.8
U.C.	+ 3.7	+ 8.2	+ 2.6	+ 8.0	− 3.0	+ 3.9
13	+ 2.8	+ 7.3	+ 5.0	+ 5.2	− 0.8	+ 3.9
14	− 0.4	+ 4.0	+ 4.1	+ 4.0	+ 1.0	+ 2.5
15	+ 0.4	+ 3.1	+ 3.0	+ 4.8	+ 2.5	+ 2.8
16	− 1.6	+ 0.8	+ 0.5	+ 3.2	+ 6.5	+ 1.9
17	− 3.2	− 1.8	+ 2.2	+ 3.6	+ 6.4	+ 1.4
18	− 3.8	− 3.2	+ 0.3	+ 0.1	+ 8.7	+ 0.4
19	− 3.4	− 3.3	− 2.0	− 2.2	+ 6.0	− 1.0
20	− 2.1	− 2.6	− 6.2	+ 0.6	+ 7.8	− 0.5
21	− 2.2	− 3.1	− 5.3	− 2.2	+ 5.3	− 1.5
22	− 2.6	− 5.7	− 2.2	− 3.3	− 0.7	− 2.9
23	− 3.8	− 7.7	− 0.6	− 1.8	− 2.1	− 3.2
24	− 1.4	− 6.4	− 0.7	− 1.4	− 5.1	− 3.0

Curves have been plotted showing the mean diurnal variation for the five series and the mean diurnal variation of potential-difference for the solar days from August 1, 1920, to May 31, 1921. It will be seen that the moon has about one-seventh the effect of the sun in producing the observed variations. It is for this reason that the irregular disturbances due to unknown causes make the lunar curve much more irregular than that due to the sun.

If the variations described are due to the electrical induction of the sun and moon, the moon must have a negative charge of an intensity somewhat less than one millionth that of the sun's charge. It seems almost certain that if the sun and moon have the enormous charges indicated by these observations the earth must also have a very great negative charge.

When these variations have been reported at previous meetings of the Society they were compared with the diurnal variations in the North magnetic component of the earth's field. It has been known for a long time that there are also variations in the earth's magnetic elements due to the moon's influence. Thus Chapman says in Phil. Trans., 213, 279–321 (1913): "The magnetic elements show regular periodic changes depending on the lunar hour angle,

just as on the solar hour angle; the latter variations are considerably the greater of the two, and almost entirely mask the lunar variations."

The above statement applies equally well to the variations in electrical potential-difference now under consideration.

STANFORD UNIVERSITY.

EARTH CURRENTS AND THE SUN'S INDUCTION.

BY FERNANDO SANFORD.

BY means of a comparison between the records of earth currents and of magnetic disturbances begun at the Greenwich Observatory in 1865, Airy was able to decide that the irregular magnetic disturbances were certainly due to earth currents and that the regular, diurnal magnetic variations were probably due to the same cause.

The relation between the diurnal variations in the two phenomena is obscured by the fact that the changes in the earth currents precede the corresponding variations in the magnetic elements by considerable periods of time. This fact is shown in Fig. 1,[1] in which the continuous curve shows the mean diurnal variation in the N–S earth current at Tortosa, Spain, for the year 1910, and the broken line shows the mean diurnal variation in the magnetic declination for the same period. The curves are drawn from the data given in the annual report for that year of the Observatorio del Ebro, at Tortosa. It will be seen that while the curve for variation in magnetic declination is very similar in shape to the earth current curve, it lags behind it in time by about three hours.

A similar lag in the diurnal variation in potential-difference between the earth and an uncharged, insulated conductor which is kept in an earthed metal cage and the diurnal variation in the north magnetic component is shown in the simultaneous records of the two phenomena made at Palo Alto during the month of March of the present year. In Fig. 2, the continuous line shows the mean diurnal variation in potential-difference between the earth and the insulated conductor, and the broken line shows the simultaneous variation in the North magnetic component.

In the extensive study of earth currents made at Berlin from 1884 to 1888, Weinstein was able to show that "almost the whole of the variation which we are able to observe by magnetometers is due to earth currents." Secular changes in the magnetic elements have not been related to earth currents.

Weinstein made another observation, the importance of which he seems not to have recognized. He stated that the general direction of the resultant earth current at Berlin is toward the sun. This must mean that the electrons in the earth regularly flow from that region of the earth nearest the sun.

In Fig. 3 the mean hourly values of the resultant *Negative* summer current at Berlin are represented in their relative directions and magnitudes by the arrows starting at distances of 15 degrees apart from the parallel of latitude of Berlin. That is, they are drawn in the directions and relative magnitudes

[1] Curves not here included.

which they had at Berlin at the hours specified on the chart. If the currents could remain stationary in the positions represented without being carried around by the rotation of the earth, the observed diurnal variation at Berlin would result. This is approximately what must occur if the currents are caused by the sun's electrostatic induction. In that case the chart represents approximately the direction and relative magnitude of the total electronic current around the 52nd parallel when it is noon at Berlin.

It will be seen that the electrons are everywhere flowing away from the part of the earth nearest the sun, and that their movement away from this region is greater on the side which is approaching the sun than on the side which is receding from the sun. The electrons are apparently repelled by the sun, and hence follow the sun around the earth, keeping as nearly as may be on the opposite side.

Since in the summer time, when these currents were observed, the part of the earth nearest the sun was about 40 degrees south of Berlin, the north component of the current predominates at noon, while at midnight, when the sun is on the opposite side of the earth and the nearest direction to its vertical rays is northward, the direction of the current is due south.

If the earth currents are due to the sun's electrostatic induction, there should be a correspondence between the diurnal variations in magnitude of the two phenomena. Since simultaneous measurements of the two phenomena have not been made at the same place, the only comparison that can now be made is between the diurnal variation of the sun's induction at Palo Alto and the diurnal variation in the total earth current at some other place.

This is done in Fig. 4, where the diurnal variation in magnitude of the total summer earth current at Berlin is represented by the continuous line and the diurnal variation in potential-difference between the earth and the insulated conductor for the month of August, 1920, is represented by the broken line.

Stanford University.

The Sun's Charge: A Criticism of Methods.

By F. J. Rogers.

In abstracts[1] of papers presented before the American Physical Society, Prof. Sanford has given experimental results obtained in an attempt to measure the diurnal variation of the earth's potential, presumably caused by the rotation of the earth in an assumed electrical field due to the sun.

I. If the earth and sun were charged alike then the electrical field near the earth would be subject to a diurnal variation, being weaker in the day-time and stronger at night. The *potential* of the earth, however, assuming it to be a conductor, would not be changed by its rotation in the field of the sun.

II. Professor Sanford's method consisted in measuring the variation in the potential difference between the earth and an insulated conductor "by means of a quadrant electrometer, one pair of whose quadrants is connected to the

[1] Phys. Rev., Vol. 17, pp. 243, 517, 1921.

water system of Palo Alto while the other pair is joined to an insulated capacity enclosed in an earthed metal cage." It was apparently expected that the potential of the insulated conductor would not change by the same amount as the expected change in the potential of the earth and the earthed screen.

If the insulated system consisting of the quadrants and the conductor connected to them is surrounded by an efficient screen, then no change in potential of the screen and the other quadrants connected to it will produce any field or difference of potential inside the screen. This conclusion follows as a necessary result from Gauss's theorem or from one of Faraday's famous experiments. The writer tested this conclusion experimentally as follows: The screen containing the electrometer, battery, and insulated conductor was set upon insulating supports and its potential was suddenly raised by 30,000 volts by means of sparks from an electrical machine, no perceptible motion of the electrometer needle could be observed. Of course this experiment will not succeed unless the screen is an efficient one, all parts of which change potential by the same amount. Reason will be given later to show that it would not succeed with Prof. Sanford's set up of apparatus.

III. An electrometer and an insulated conductor connected as described does give a diurnal variation of the electrometer deflection. There are at least three causes for such a variation, which are located inside the screen.

1. When the quadrants are insulated the needle "drifts" towards a "false zero"; this zero is not stable but itself varies. The cause of the drifting is a minute ionization current from the charged needle to the quadrants and a leakage current from quadrants to ground.

2. If the potential of the needle changes while one pair of the quadrants is insulated, there will be a proportionate change in the potential difference between the quadrants. If e is the potential difference between the quadrants (starting from zero) and ΔE is the *change* in potential of the battery charging the needle, it may be easily proved that

$$e = \frac{C}{C + C_0} \Delta E$$

in which C_0 is the capacity of the insulated quadrants and the conductor connected to them and C is the capacity between the insulated quadrants and the needle. The e.m.f. of the battery necessarily has a diurnal variation on account of the diurnal change of temperature.

3. The insulated quadrants and the conductor connected to them form one coat of a condenser the other being the electrometer case and the earthed screen. When the quadrants are earthed this condenser becomes charged by the contact e.m.f. between the two coats, producing a weak electrical field between the opposing surfaces. Upon insulating the quadrants this field immediately begins to disappear on account of residual conductivity induced by radio activity or some other cause. This change of potential depends primarily upon the value of the contact e.m.f. but the *rate* of change depends

greatly upon the condition and temperature of the opposing surfaces. In particular if the conductor is freshly sand-papered aluminum the change of potential after insulation is at first quite rapid but as the aluminum tarnishes the rate of change (starting from zero each time) becomes less and less, and finally becomes very small. An aluminum plate which had never been sand-papered (or otherwise "sophisticated") changed its potential very slowly after being insulated, but this rate of change was enormously increased by a considerable rise in temperature, quickly returning to its original value as the original temperature was regained. It is quite obvious that such a condition provides a cause for change of potential which, at least in part, explains Prof. Sanford's experimental results.

IV. It has been assumed so far that Prof. Sanford's screen is an efficient one. That this is not the case is demonstrated by the fact that a passing street car (too distant to produce any mechanical effect) makes a perceptible deflection of the electrometer needle. It appears that the metallic screen surrounding the insulated conductor does not extend *under* it. The ground itself is depended upon to be sufficient. Now the ground and the water pipes are not at the same potential and what is more important, the potential of these two 'grounds" do not change at the same rate or by the same amount. Any change in the relative potential of ground and water pipes, produced by a passing street car or other earth currents will produce an electrometer deflection. Thus the imperfection of Prof. Sanford's screening allows him to obtain an effect in part due to potential differences in the ground, which are directly associated with earth currents. I believe that, in general, these effects are extremely small as compared with the disturbances due to the other causes already mentioned.

All the statements above made have been substantiated by profuse experimental results which will probably be published later.

Stanford University.

The Effect of Temperature on the 3883 CN Band.

By Raymond T. Birge.

A study of furnace spectrograms of the 3883 CN band,[1] kindly lent to me by Dr. King, and of ordinary arc exposures of my own, has furnished some new evidence in connection with the quantum theory of band spectra, as developed by Heurlinger and others. The chief point in this theory is the similarity of the positive and negative branches of the series forming each sub-head of the band, the common origin of the two branches being taken at the point of zero intensity of the "singlet" series. In the A_1 series this is at λ 3875.342, for which $m' = 28$ by the usual nomenclature, or $m = 0$ by the new nomenclature. The A_2 series is theoretically a portion of the negative branch and is simply a continuation of the A_1 series.

[1] Astrophysical Journal, 53, 161, 1921.

By comparing lines of equal photographic blackening, on arc exposures of varying length, there has been obtained, for the first time, a quantitative curve of the intensity distribution in each branch of the A series. Using only "free" lines, the curve is *smooth* and *regular* throughout, even for perturbed lines, and is quite different in shape from Haferkamp's plot.[1] Within limits of error, the *shape* of the curve is quantitatively the *same*, for the positive and negative branches, but the negative branch is about 15 per cent. stronger. The phenomena is similar to that shown by infra-red bands, for which a theoretical intensity formula has been derived by Kemble.[2] This formula ($I = c_1 m e^{-c_2 m^2}$) does *not* hold for the author's curve. But the modified formula $I = c_1 m^{3/2} e^{-c_2 m^{3/2}}$ holds within limits of error (about 10 per cent.) from $m = 4$ to $m = 137$. This covers an intensity variation of 60,000 per cent. The maximum intensity is at $m = 30.4$ and hence the especially strong head of this band is due to the accidental coincidence of the maximum of intensity of the negative branch and the vertex of the $\nu : m$ curve.

The arc spectrograms of King, taken with 170 volts, 4 amperes, show a definitely different intensity curve from those of the author, taken with 170 volts, 13 amperes. The maximum is shifted to about $m = 28$, but the equation quoted still seems to hold. In the case of the *furnace* spectrograms (taken at 2700° C., 2500° C., and 2300° C.) there is a *radical* redistribution of energy, the maximum being shifted to $m = 22$ or less, and the higher values of m having far less intensity. This is to be expected on quantum theory, as the value of m is proportional to the number of quanta of angular momentum possessed by the radiating molecule, and this number should vary with temperature. *In all cases*, the positive and negative branches seem to have the *same* shape, the negative being however slightly stronger. It is difficult to get any accurate criteria for judging the relative intensity of the self-reversed lines of the furnace spectra, and it is not certain, thus far, whether the formula quoted holds for these spectra.

The enhancement of the A_1 series over the A_2, as noted by King, is thus due to a *similar* redistribution of energy in the positive and negative branches of the general A series. Similar phenomena are shown by the B and C series. Because of these energy changes, it is possible to further analyze certain perturbations. The results for the A series show that in all cases the perturbations occur in pairs at m and $-(m+1)$, and are similar, agreeing with Bachem's recent results from magnetic effects.

A careful study of the head of the band shows that it is possible to assume that the *doublet separation* is the *same*, for *corresponding* members of the two branches, and that this separation decreases linearly to zero, at $m = 0$, from the last resolvable doublet at $m = 28$. The first members of the A_1 and A_2 series coincide to less than 0.002 Å, at the "head" of the band (3883.4), and the value of $\Delta\nu$ for A_1 and A_2 is the same at this point, showing that A_2 is a smooth continuation of A_1, in every respect, as demanded by theory. How-

[1] Zeit. wiss. Photographie, 9, 19, 1910.

[2] PHYS. REV., 8, 689, 1916.

ever, the values of A_2–A_1, using the *mean* frequency of each doublet, and using a newly discovered A_2 doublet $m = 77$, show that the complete $\nu : m$ curve is *not* symmetrical with respect to a line $m = c$, as demanded by Thiele's theory. Imes has found similar dissymmetry for the infra-red bands.

A series of very faint doublets, as mentioned by King, appears in the furnace spectra, but not in any arc spectra I have seen. (However, Kayser and Runge seem to have obtained these lines in the arc, and measured them, as single lines. Uhler and Patterson did not obtain them.) I have succeeded in measuring six of these doublets, and using the mean frequency of each doublet they fit, with an average error of 0.0004 Å (purely accidental accuracy) the Deslandres' formula $\nu = 25,750.175 + 0.017143\,(m + 0.3232)^2$ where $m = 25$ to 30. This gives the vertex of the parabola at 3882.37 Å, but if the series deviates from Deslandres' law as does the A_1 series, the "phase" would be practically zero, and the head at about 3881.47 Å. The doublet separation is the same as that of neighboring A_2 lines. This new series is seemingly not accounted for, in the quantum theory. The theoretical "zero" branch of the A series should have the vertex of the parabola at λ 3874.906.

This investigation is still in progress and some of the above results are to be considered as provisional.

PHYSICAL LABORATORY,
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SOME X-RAY ISOCHROMATS.

BY DAVID L. WEBSTER.

THIS paper is a preliminary report on a study of the x-ray isochromats of different metals in different directions, that is being made as a first step toward the law of intensity as a function of potential, frequency and direction, by a method previously described. The present report deals with wave-lengths 1.0 to 0.3 Å, as obtained from tungsten at 50° and 140° from the line of the cathode rays, and from copper at 55° and 145°, the latter metal being the target in a special Coolidge tube furnished by the General Electric Co., through the kindness of Dr. Coolidge.

The graphs are of the same general type as those previously published for other conditions, with only slight deviations from the author's empirical formula,

$$I(V, \nu) = k(\nu)\left\{(V - H\nu) + H\nu p(\nu)\left(1 - e^{-q(\nu)(V/H\nu)-1}\right)\right\},$$

but no exact statements can be made until several sources of error are eliminated. One of these errors, due to absorption in the target, is worth noting here, because the only direct experimental evidence previously available on that point was in the form of spectrum graphs. These graphs show no discontinuities in the general radiation at the absorption limits, except in

[1] See Bulletin of the National Research Council, Vol. 1, Part 7, Dec., 1920.

special cases, where the rays used were ones leaving the target at a small angle to its surface, and the target was known to be rough. From this one would infer that absorption in the target is relatively unimportant except in those special cases, and that even there it is likely to be an almost constant factor, depending on the shapes of the minute irregularities in the surface. But some evidence to the contrary now appears in some isochromats taken at different angles from the surface of the target but at the same angle from the cathode rays. These isochromats show differences of a sort suggesting variable absorption in the target, at least when the angle of the x-rays from its surface is small. The theory of this absorption is complicated by the fact that the cathode rays do not go straight within the target, as well as by the most minute roughness in the target, but it ought to be possible to determine the absorption factors experimentally, by reference to the absorption limits as shown in the emission spectra under different conditions.

STANFORD UNIVERSITY.

THE WIDTH OF X-RAY SPECTRUM LINES.

BY ARTHUR H. COMPTON.

THE width of x-ray spectrum lines is ascribed to (*a*) the width of the slits employed, (*b*) angular imperfections of the crystal, (*c*) finite resolving power of the crystal grating, and (*d*) lack of homogeneity of the x-rays. Experimental values of the width of the tungsten lines $\lambda = 1.242$ and 1.279 Å.U. in the first four orders from the cleavage faces of rock-salt and calcite are given. Analysis of the data indicates that each of the above factors contributes measurably to the observed width. In particular the average lack of homogeneity of the lines is found to be $\delta\lambda/\lambda > 0.0007 \pm .00013$. This result is in accord with the complexity of the lines as predicted by Sommerfeld's theory of elliptic electronic orbits.

WASHINGTON UNIVERSITY,
ST. LOUIS, MO.

THE EFFECT OF DAMPING ON THE WIDTH OF X-RAY SPECTRUM LINES.

BY G. E. M. JAUNCEY.

IT is assumed that the ether vibrations due to an oscillator giving out x-rays can be represented by

$$y = e^{-kt} \sin (pt + A).$$

Developing this as a Fourier integral, a relation between the damping factor k and the width of the resulting spectrum line is found. To obtain the experimental widths of x-ray spectrum lines found by A. H. Compton, k must exceed $5.3 \times 10^{+5}$ sec.$^{-1}$ for the wave-lengths used, while on electrical theory the damping factor of an oscillator giving out radiations is 7.2×10^{14} — sec.$^{-1}$ for this wave-length. The damping therefore accounts for something less than

one seventh of the width found. The width due to damping for any wavelength is 1.2×10^{-4} Å.U.

WASHINGTON UNIVERSITY,
ST. LOUIS, MO.

EXPERIMENTS ON POLARIZATION OF X-RAYS.

BY PAUL KIRKPATRICK.

FORMULÆ expressing the intensity of reflection of x-rays from crystals contain a term sometimes referred to as the "polarization factor." It is of the form $(1 + \cos^2 2\theta)$, where θ is the angle of reflection. This term is the summation of the squares of the amplitudes of the components of the electric vector respectively normal to and in the plane of reflection, the normal component of the vibration of the radiating oscillator being equally effective for all values of θ, while only a projection of the component in the plane of reflection is effective, this projection diminishing with the cosine of the angle of deviation, or 2θ. It is seen that with θ small, as it ordinarily is, the degree of polarization of the reflected beam is also quite small.

However the polarization factor as stated above becomes incapable of predicting the degree of polarization in any experimental case for two reasons. The original ray from the ordinary x-ray tube is not free from polarization. In consequence we must write the polarization factor $(1 + A \cos^2 2\theta)$, A becoming unity only when the line joining the electrodes within the tube makes an angle of 45° with the plane of reflection. Further, the ordinary form of the polarization factor ignores the possibility of multiple reflection within the crystal, in consideration of which we should write $(1 + \cos^{2n} 2\theta)$, wherein is the number of reflections undergone before emergence from the crystal. This form of the factor leads us to expect a higher per cent. polarization than that predictable from the simpler form.

Apparatus has been constructed for measuring polarization by successive reflection of x-rays from two crystals variously oriented. The method is analogous to that used for exhibiting polarization of light by reflection from two glass plates. The twice reflected ray is received in an ionization chamber and the total ionization is recorded by a string electrometer as the second crystal is swept across its position of reflection. Rough preliminary measurements show a tube polarization in the expected direction. In investigations of crystal polarization the intensities in the parallel and crossed positions have been found sensibly the same for angles of reflection less than eight degrees.

DEPARTMENT OF PHYSICS,
UNIVERSITY OF CALIFORNIA.

AN X-RAY SPECTROMETER FOR THE DETERMINATION OF ABSORPTION COEFFICIENTS

BY ELMER DERSHEM.

THIS x-ray spectrometer is equipped with a high grade circle and micrometer eyepieces such as to make readings possible to one or two seconds of arc. A string electrometer is attached to the ionization chamber and rotates with it, thus eliminating changes of capacity. The electrometer has a sensitivity of about 75 divisions per volt while the electrical capacity of ionization chamber and electrometer combined is only 13 centimeters. By the use of amber insulation and specially purified and dried methyl iodide gas the blank leak is made entirely negligible in comparison with the rate of motion of string during readings.

When used in connection with a carefully regulated Coolidge x-ray tube one is able to measure absorption coefficients of any material for homogeneous x-rays with a probable error of less than 0.05 per cent.

DEPARTMENT OF PHYSICS,
UNIVERSITY OF CALIFORNIA.

A PHOTOGRAPHIC METHOD OF X-RAY CRYSTAL ANALYSIS.

BY ELMER DERSHEM.

WHENEVER the x-ray analysis of crystals by the photographic, crystal rotation method is undertaken, many curved lines or streaks, some of them very sharply defined, appear on the plate if it is sufficiently large. The position and length of these lines depends entirely upon the slopes of the reflecting planes in the crystal and the angular rotation of the crystal during exposure. It is possible with a single exposure to determine the distance between certain planes parallel to the axis of rotation by the spacing of characteristic lines and from the same plate the slopes of other planes with respect to the first and therefore to be able to determine the shape and volume of the elementary parallopipeda of the crystal lattice.

Formulæ are derived giving the locus of points on these lines in terms of the measured rotation of the crystal and the indices of the reflecting planes. For any assumed space lattice it is possible to compute the locus of these lines and check with the photograph. This method should be useful in the case of crystals which, on account of small dimensions in certain directions, *e.g.*, thin lamellar crystals, do not reflect well enough to give line spectra from all the possible faces.

DEPARTMENT OF PHYSICS,
U IVERSITY OF CALIFORNIA.

SECRET PHOTO-ELECTRIC SIGNALLING.

BY ELMER DERSHEM.

A DESCRIPTION and demonstration of an apparatus for signalling consisting at the sending end of a source of light and a rotating disc having a different

number of sectors at different distances from the center but having the ratio of open to closed segments the same for all radii. If the sector disc is moved across the beam of light the total intensity remains constant and hence an unequipped observer is unaware of any change as the interruptions are too frequent to be noted by the eye. At the receiving station this beam which has been interrupted 500 to 1,000 times per second falls upon a photo-electric cell connected to a multiple stage audion amplifier and the signals, made by moving the disc across the beam, may be heard as changes in pitch in the telephones. Tests have shown that a light intensity equal to one per cent. of that of the full moon is sufficient for this purpose without condensing lenses while with their use the necessary intensity is less, depending upon the size of the lens.

DEPARTMENT OF PHYSICS,
UNIVERSITY OF CALIFORNIA.

AN HARMONIC CURVE WRITER.

BY WILLIAM J. RAYMOND.

THE Harmonic Curve Writer, briefly described at a meeting of the Physical Society,[1] has now been completed. The scope of the machine has been considerably extended by means of attachments, so that the visual representation of types of vibration, other than those originally planned, has been made possible.

In the machine as now constructed there are four vertical shafts, each carrying a driving cone. By means of friction wheels, which transmit the motion from cone to cone, four relative frequencies of rotation are possible, which may have any desired values between 1 and 27. Each shaft actuates a slotted cross-head, and by means of a summation-wire passing over pulleys, the vibratory motion of the cross-heads, doubled in amplitude, is communicated to a tracing pen. Circular motion of the pin which drives a cross-head causes simple harmonic motion. Spiral motion of the pin, obtained by an independently driven cam, causes damped harmonic motion, the value of the decrement depending upon the relative frequencies of rotation of the cam and cone-shaft. Equiangular spiral cams have been made for logarithmically damped motion, and Archimedean spiral cams for rectilinearly damped motion. The initial amplitude of one of the four component motions, given to the tracing pen, may have any value within 7.5 cm.

The pen moves transversely across a band of paper 30 cm. wide, which is driven at constant speed from one roller to another. With this arrangement the curve writer may be used in the following ways: (1) It will draw sinusoids of amplitudes less than 7.5 cm. and wave-lengths between 0.25 cm. and 125 cm. (2) It will draw damped sinusoids with a wide range of decrements. (3) It will combine two to four sinusoids of commensurable or incommensurable wave-lengths, as, for example, the representation of the four principal harmonics

[1] PHYS. REV., Vol. XI., p. 479.

of a bell-tone. (4) It will combine damped sinusoids, drawing curves which represent the vibrations of coupled, oscillatory systems, mechanical or electrical. (5) It will combine two decrescent, exponential curves, representing over-damped or ultra-periodic motion. (6) It will combine two ultraperiodic curves, or an ultraperiodic curve and one or two damped sinusoids. (7) It will combine damped and undamped sinusoids, to represent forced vibrations of mechanical systems, or the so-called starting-currents in certain electrical circuits.

As an attachment to the machine, a rotating circular plate may replace the band of paper, to receive the record of the tracing pen. With a wide range of frequencies of rotation, in terms of the period of the pen, many of the curves drawn by the older harmonographs may be reproduced. The trace of the pen may pass through the center of the table, or along a line parallel to a diameter.

A second attachment consists of a square table, rolling to and fro on rails, in a direction perpendicular to the motion of the pen. One or two of the slotted cross-heads may be diverted from their usual function of operating the pen, to produce simple or complex harmonic motion of the table. When two cross-heads drive the pen and two the table, the Duplex Harmonograph of Vincent and Jude[1] is imitated. A number of their more striking curves have been drawn, as well as some of the simpler forms originating with Lissajous.

DEPARTMENT OF PHYSICS,
UNIVERSITY OF CALIFORNIA.

THE VARIATION OF THE THERMAL CONDUCTIVITY OF SOFT CAST IRON WITH THE TEMPERATURE.

BY ELMER E. HALL, O. R. HULL AND O. S. IMHOFF.

USING for the specimen a cylindrical shell capped by a hemispherical shell, the authors have measured the conductivity of a given casting of soft iron, such as used for stoves, at various temperatures in the range 190° to 540° C. Special attention was paid to securing radial flow, to the construction of the thermocouples, and to measuring the energy input. The difference in temperature between the inside and outside of the specimen was usually three or four degrees. The conductivity increased from 0.07 at 195° to 0.20 at 542°.

DEPARTMENT OF PHYSICS,
UNIVERSITY OF CALIFORNIA.

THE INDEX OF REFRACTION OF WATER, ETHYL ALCOHOL, AND CARBON BISULPHIDE AT VARIOUS TEMPERATURES.

BY ARTHUR R. PAYNE AND ELMER E. HALL.

THE index of refraction of water was measured by the spectrometer method from 16° to 98.4° C., observations at thirty-four different temperatures in this range being made. Special attention was paid to the region above 50°. Precautions were taken to secure uniform and constant temperature during

[1] Phil. Mag., 6 Ser., Vol. XXIX., pp. 490–514, Pl. VIII.

a set of readings. Angles were read to seconds. The prism was a specially designed gold plated brass prism with optical glass sides. Before gold plating the brass prism it was found that enough impurity dissolved in the water in a few hours to change the index by two units in the fourth decimal place. The variation of the refractive index with temperature is given at various temperatures throughout the range studied. The results are compared with those of previous workers. The results of similar measurements are given for ethyl alcohol for the temperature range 15° to 75°, and for carbon bisulphide for the range 16° to 45° C.

DEPARTMENT OF PHYSICS,
UNIVERSITY OF CALIFORNIA.

PRELIMINARY REPORT ON SPECTROSCOPIC INVESTIGATIONS IN THE EXTREME ULTRA-VIOLET.

BY J. J. HOPFIELD.

A METHOD has been developed for making Schumann films suitable for work in the extreme ultra-violet. These films can be developed at room temperature for ten minutes and longer and still show no trace of fog.

A method has been devised for obtaining the emission spectrum of highly absorbing gases even below the limit of fluorite absorption. The method consists in keeping the receiver of the vacuum spectrograph filled with hydrogen or some non-absorbing gas, while the discharge tube of internal capillary end-on type is filled with the gas under investigation. The two gases are kept localized by flowing constantly in contrary currents and by being continually pumped out through a common exit.

Using the above method of investigation, a very strong triplet λ 1302.5, 1305.2 and 1306.4 of relative intensities 8, 6, and 5 respectively was discovered when the vacuum tube contained oxygen and is attributed to that gas. If this is the first member of a fundamental series it corresponds to a resonance potential of 9.45 volts, a somewhat higher value than that experimentally observed.

By regulating the flow of gases so as to allow a mixture of hydrogen and oxygen or of hydrogen and air in the discharge tube, most of the secondary spectrum of hydrogen in the Lyman region was suppressed while the fundamental line λ 1215.6 and other lines, including the oxygen triplet mentioned above, were brought into prominence.

DEPARTMENT OF PHYSICS,
UNIVERSITY OF CALIFORNIA.

THE EFFECT OF PRESSURE ON THE BAND SPECTRA OF NITROGEN.

BY JEAN HUDDLESTON.

THE only work that has been done on the effect of pressure on nitrogen band spectra is that of Villari, Cailletet and Cazin, who, about 1875, observed

separately that with increasing pressure, the band spectra gradually became continuous. The object of the present investigation was to get photographic record of the changes in the spectra, and to discover at what pressure the various groups gave way to a continuous background.

A brass cylinder was first used, with a hand pump to give the increased pressure. When the spark was excited between copper electrodes by a large transformer run on 110 volts, it was found that the NO_2 formed in the cylinder produced such a strong absorption spectrum that all nitrogen bands were completely destroyed. The substitution of platinum electrodes for copper lessened the formation of NO_2 materially, and when the transformer was replaced by a small induction coil run on 8 volts, the plates showed no absorption. The other apparatus was of glass, and could be evacuated and filled with chemically prepared nitrogen, in which atmosphere no NO_2 would be formed. A 4-prism glass spectrograph was used, the range of wave-lengths recorded being from about 3700 to 5700; but since the spectrum was always faint above 5200, the bands available for study were the negative pole bands and the second group of positive bands.

The spark in pure nitrogen was submitted to pressures of 1, $1\frac{1}{2}$, 2, 3, $3\frac{1}{2}$, 4 atmospheres. At one atmosphere the positive and negative bands were of about the same strength. As the pressure increased, there was a gradual formation of a continuous spectrum, which appeared first in the longer wave-lengths, and worked on down toward the violet. At four atmospheres this hazy background had filled the entire spectrum, with band structure barely visible from 4344 to a little below 3997. Positive and negative bands seemed to be affected similarly. The continuous spectrum extended as far into the longer wave-lengths as the plate registered, but showed a decided decrease in intensity around 5200–5500.

When the spark was produced in air, in the brass cylinder, by a small induction coil run on 8 volts, the negative bands were stronger than the positive at one atmosphere. Pressures of 1, 2, 3, 4, 5, 6 atmospheres were used. With increasing pressure, the continuous spectrum gradually blotted out all band structure, closing in from the red, as before: but this change came earlier. At three atmospheres the positive bands had all given way, and the negative bands following the heads 4278 and 4236 were the only ones discernible. At four atmospheres all bands were gone; five and six atmospheres showed merely an increasingly heavy continuous background, crossed by some nitrogen and metal lines, but no band heads.

When the spark was produced in the cylinder by a large transformer run on 110 volts, the general progressive changes were much the same, except that here the continuous background was slower in forming, not blotting out all band structure until six atmospheres. Again the negative bands were stronger than the positive, and those following the head 4278 were the last to go. As in all other cases, the background had a decidedly diminished intensity around 5200–5500. At one atmosphere the maximum intensity of the band spectrum

was around 4278, while at six atmospheres the maximum of the continuous spectrum was around 4630.

The region of the first group of positive bands, which was not recorded on the plates, was observed visually, by means of a constant deviation spectroscope. There was no evidence of any band structure at one atmosphere, or at any higher pressure, that region giving an apparently continuous background in all cases. This is in accordance with the evidence on the plates, namely that the bands in the longer wave-lengths tend to give way sooner to a continuous spectrum. The first group apparently becomes continuous below one atmosphere.

DEPARTMENT OF PHYSICS,
UNIVERSITY OF CALIFORNIA.

THE REACTION OF IRON WITH NITRIC ACID.

BY JOSEPH G. BROWN.

IN previous papers the theory was advanced that the rate of solution of iron in nitric acid of different density is associated with different chemical reactions. This theory was based upon the study of a voltaic cell having an iron anode and with nitric acid as an electrolyte. In general it was concluded, (1) that the rapid rate which takes place in dilute acid is associated with the formation of ferrous nitrate, (2) that the moderate rate which occurs in acid of intermediate density is associated with a ferrous reaction involving some other product than ferrous nitrate, and (3) that the very slow rate in concentrated acid is associated with a ferric reaction.

The chemical products of this reaction and of the electrolysis of nitric acid were investigated by Freer and Higley in 1899. Veley and Manley measured the electrolytic conductivity of nitric acid in 1898. Young and Hogg measured the reaction rates of the process in 1915.

A consideration of the results of these studies and of the properties of the iron and nitrogen oxides and hydroxides has led to a more detailed theory of the action of iron with nitric acid.

Iron forms three known oxides: ferrous, ferric and ferroso-ferric; and three hydroxides: ferrous, ferric and meta-ferric. The hydroxides are amphoteric; *i.e.*, they act either as weak bases or weak acids. This indicates that they ionize either with hydroxyl or hydrogen ions and probably with both. The ease with which iron compounds change valence and the tendency which they have to form compounds with mixed valence are well known.

Nitrogen forms five oxides: pentoxide, peroxide, trioxide, nitric and nitrous, and in combination with hydrogen, amine oxide and ammonium oxide. These oxides unite with water to form the series: nitric acid, nitrous acid, hyponitrous acid, hydroxyl amine and ammonium hydroxide. Dilute nitric acid is one of the strongest acids known, while ammonium hydroxide and hydroxyl amine are bases. The intermediate compounds are weak acids.

A study of the properties of water solutions of nitric acid, of their action in electrolysis, and their reaction with metals, indicates that as the density increases the acid characteristics become weaker, and the basic characteristics become stronger, thus showing the amphoteric nature of nitric acid.

The reduction products which result when iron is dissolved in dilute acid are shown to be the consequence of the action of hydrogen ions in decreasing the valence of nitrogen. In consequence of this reduction electrons are removed from the iron by No^+ and N^+ ions. In concentrated acid, however, the hydrogen ion concentration is small, hence the reducing action upon the nitrogen does not occur. This results in electrons being removed from the iron by the No_2^+ ions, which, on account of their oxidizing character, increase the valence of the iron, thus forming ferric ions before any reaction takes place.

The observations are best accounted for by assuming that in concentrated acid the reaction is basic; *i.e.*, that the iron ions unite first with hydroxyl ions.

The products of the electrolysis of nitric acid solutions and the formation of the passive condition when an iron anode is used in the electrolysis, are in strict agreement with these conclusions.

It is believed that the principles involved in this theory are of general application. Chromium forms a series of oxides similar to iron but with an additional acid forming oxide. When chromic acid is used as an electrolyte in the cell with an iron anode, the results are similar to those obtained with concentrated nitric acid. No matter how dilute the chromic acid solution may be, there is no indication that the acid reaction takes place. This might be expected since chromium compounds show a more strongly amphoteric character and chromic acid is much weaker and more oxydizing than nitric acid.

STANFORD UNIVERSITY.

A BRAUN TUBE, UNDAMPED WAVE, PRECISION METHOD OF DETERMINING DIELECTRIC CONSTANTS OF GASES.

BY L. T. JONES AND H. G. TASKER.

AN undamped wave method of measuring small capacities has already been announced by Hyslop and Carman.[1] It has the disadvantage, however, of being applicable only to determining the dielectric constants of liquids, the sensitivity not being sufficiently great to measure smaller increments of capacity with the needful accuracy.

The new method combines all of the advantages of their arrangement but departs therefrom in the use of a Braun tube oscillograph in making frequency comparisons, by which means frequency ratios (of measuring and reference circuits) in any small whole numbers up to 15 may be determined with an accuracy of .05 cycle.

The method further departs from all others heretofore used for the measurement of changes in capacity, in that the desired value is determined without readjusting the circuits in any manner. This is accomplished by observing

[1] PHYS. REV., XV., p. 243, 1920.

the frequency change in cycles as indicated by the changing Lisajous figures on the Braun tube and interpreting this quantity mathematically.

It is found that the change in capacity (ΔC) produced by introducing gas to the test condenser may be expressed thus:

$$\Delta C = \frac{-1\left(\frac{2\Delta f}{f_0} + \frac{\Delta f^2}{f_0^2}\right) C_0}{1 + \frac{2\Delta f}{f_0} + \frac{\Delta f^2}{f_0^2}},$$

where C_0 = initial capacity of measuring circuit,
f_0 = initial frequency of measuring circuit,
and Δf = change in frequency of measuring circuit.

This equation is rigidly accurate but if f_0 exceeds 500,000 and Δf does not exceed 50, as will probably be the conditions of the work, then an error of less than .03 per cent. will be introduced by writing the equation thus:

$$\Delta C = \frac{-2\Delta f C_0}{f_0},$$

whereupon we have

$$K - 1 = \frac{-2\Delta f}{f_0} \times \frac{C_0}{C_v},$$

where C_v is the capacity of the test condenser with vacuum as dielectric.

It is obvious, then, that this method measures not K but the excess of K over unity, and that the accuracy of this measurement depends upon the relative rather than the absolute accuracy with which C_0, C_v and f_0 may be measured. The capacity sensitivity should be about 10^{-16} farads or 10^{-4} cm.

The authors propose to employ the method in one or more of the following investigations:

1. To obtain new and more accurate values of K for several gases.
2. To investigate variations of K with pressure of the gas.
3. To discover, if possible, a dependence of K on some molecular property.
4. To investigate variations of K with temperature.

In addition it may be used in any connection requiring the measurement of a very small capacity.

Department of Physics,
University of California.

The Effect of Ultra-Violet Light on the Viscosity of Rubber Colloids.

By Richard Hamer.

During some research work on rubber colloids for the Honorary Advisory Council for Industrial and Scientific Research, Ottawa, Canada, the writer subjected a solution of Para rubber in pure benzol, to exposures of different lengths of time, and different limiting wave-lengths of ultra-violet radiation.

The periods taken for 34.2 c.c. to pass through a fine capillary tube at a constant temperature of 30.0° C. before and after the treatment, gave the viscosity relative to the initial reading taken as the standard.

The experimental results indicated that the radiation had a marked effect in decreasing the viscosity. The effect was cumulative with the time, and somewhat progressive after the radiation had ceased.

Radiation of shorter wave-length seemed more effective than that of longer wave-length.

The writer suggests that the cause lies in a depolymerizing effect of the radiation on the rubber particles.

The investigation is being continued for the purpose of following up some of the interesting points suggested.

UNIVERSITY OF CALIFORNIA.

THE SIMPLEST MERCURY VAPOR PUMP.

BY L. T. JONES.

SINCE the mercury vapor vacuum pump was first produced by Gaede it has rapidly taken its place as the most satisfactory of all pumps for the production of extremely high vacua. The quest may well be continued till not only the simplest form has been devised but also until one is designed that will pump against a very considerable back pressure.

The pump here described is like its predecessors in that the supporting pump must be capable of producing a vacuum of about .001 mm. Exhaustion will then be completed as far as adsorption of air by the vessel will permit.

A bulb containing about 25 c.c. of mercury is heated by a bunsen burner and the vapor rises through a nozzle to a chamber surrounded by a water jacket. The air intake is situated a little below the end of the nozzle but above the lower end of the water jacket. The air inlet tube is taken out through the side of the water jacket. After condensation the mercury drops down outside the nozzle and is readmitted to the heating chamber by a device first described by Knipp.[1] A forepump removes the air from the top.

The pump is made entirely of Pyrex glass and indeed cannot be made of any higher coefficient glass. A moderately skilled glass blower can make one in considerably less than an hour. The one demonstrated was made by the author in thirty minutes.

A more detailed description will be given at a later date.

DEPARTMENT OF PHYSICS,
UNIVERSITY OF CALIFORNIA.

A NEW ROTARY MERCURY PUMP.

BY L. T. JONES.

THIS pump is a liquid piston pump with mercury level remaining constant. A cylindrical housing closed by an iron plate and mercury seal and containing

[1] PHYS. REV., 9, p. 311, 1917.

the rotating drum is divided by a baffle plate into two compartments, the low vacuum and the high vacuum. The rotation of the iron drum forces the air from the high vacuum side along the axis of the drum to the low vacuum side where it is removed by an auxiliary pump. This auxiliary pump should be capable of producing a vacuum of about 1 mm.

Both the inlet and outlet connections are at the top of the main housing and are mercury sealed in a very simple manner. The shaft, entering below the mercury level on the low vacuum side, is provided with a mercury seal. The drum is of cast iron and freedom from breakage enables one to do away with elaborate glassware to separate the two chambers when the exhaustion has reached a certain stage.

The general performance is of the same order as that of the Gaede pump. The chief advantages lie in its sturdiness, the size of the intake and its smaller cost of construction. The experimental work is not yet completed.

DEPARTMENT OF PHYSICS,
UNIVERSITY OF CALIFORNIA.

ATOMIC RADII.

BY MAURICE L. HUGGINS.

A COMPARISON of "atomic volumes" is of much less value than a similar comparison of "atomic radii." W. L. Bragg has recently[1] shown how, from our present knowledge of crystal structure, it is possible to compute values of atomic radii for many of the elements, these values being fairly consistent in different crystals. His methods, however, are only applicable to those cases in which the electron bonds are on the center lines between adjacent atoms, if we identify (as we must in order to obtain even approximate constancy for a given element) the atomic radius with the distance from atomic center to valence electron group. It is necessary, then, before computing these distances, to know the arrangement of valence electrons in the crystal. In cases where we know the arrangement of the atoms, the orientation of the electrons can be arrived at by the proper use of the Lewis theory of valence and atomic structure. A few examples illustrating the method in simple cases were given.

The various factors affecting the distance between atomic center and valence electron groups were briefly discussed, with examples.

DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA.

STRUCTURE OF THE L-SERIES OF TUNGSTEN AND PLATINUM.

BY FRANK C. HOYT.

FOR the purpose of investigating the L-series of x-ray spectra a vacuum spectrograph has been constructed capable of furnishing very high dispersion.

[1] Phil. Mag. (6), 40, 169, 1920.

This was made from a piece of 10-inch iron pipe 10 feet long with a large calcite crystal mounted at one end, the whole being sealed by iron face plates bolted on the ends. In one of these a slit about 1 mm. wide, covered with paper, was provided for the entrance of the rays from the x-ray tube outside. Both tube and crystal were movable about a common center, so that the reflected beam could always be sent straight down the pipe. With a good oil pump a vacuum of about $\frac{1}{2}$ cm. of mercury could be maintained. A series of lead diaphrams provided excellent screening from stray radiation. At one setting of the crystal a spectrum covering about .2 Å. could be photographed, with a dispersion of about .018 Å./cm.

This arrangement is not adapted to direct wave-length measurements, but the values for lines near known ones can be found by interpolation with a certainty of about .2 per cent. The very weak lines in the β-groups of Pt and W have been measured in this way, and the results are given in the table below. The absorption spectrum of tungsten was photographed on the same plate as the emission spectrum by interposing a screen of sodium tungstate. The values thus obtained for the wave-lengths of the discontinuities have no very great accuracy, but with the high dispersion employed their positions relative to the weak lines can be determined, and this is of some theoretical importance.

Tungsten.

Interpolated Value.	Reported Value.	Notation.
1.236 Å.	1.2395 (Siegbahn[1])	
1.221	1.2205 (Siegbahn[1])	Webster, β_6; Coster, β_7
1.213	1.213 (Overn[2])	
1.209	1.209 (Overn[2])	
1.201	1.2031 (Siegbahn[1])	Siegbahn, β_5.
1.212	1.2140 (Duane and Patterson[3])	La_1 absorption limit

Platinum.

1.079 1.077	1.078 (Coster[4])	Webster, β_6; Coster, β_7
1.070	1.0701 (Coster[4])	Siegbahn, β_5.
1.059		
1.053		

Duane and Patterson[5] have reported that the critical absorption wave-length La_1 in tungsten is about .8 per cent. *longer* than that of the emission line β_5. This does not seem to be altogether in accord with present theories of emission, as β_5 has been found to have a critical potential equal to the quantum potential of the absorption limit La_1[2,3]. Here the discrepancy is

[1] Phil. Mag., 38, 639, 1919.
[2] PHYS. REV., 14, 139, 1919.
[3] Ibid., 16, 526, 1920.
[4] Z. Physik, 4, 178, 1921.
[5] PHYS. REV., 16, 526, 1920.

not real, however, for the line which is just on the short wave-length side of La_1 is not the line assigned to L_1 in tungsten,[1] which was the line at 1.2118 Å. For some reason this line at 1.2118 Å. does not seem to have been observed by Duane and Patterson, although on photographic plates it is fully as strong as the line at 1.2031 Å. which they have taken as β_8, following Siegbahn.[2] That the line at 1.2118 Å is the one that corresponds to β_8 in the other heavy elements has already been pointed out.[3] This line is quite near to the absorption limit La_1 as measured by Duane and Patterson and the high dispersion picture showed it almost coincident with the lines at 1.209 and 1.213 Å, which constitute the doublet into which the 1.2118 Å line separates. Whether it was between them or on which side could not be determined with certainty, as the emission lines were very weak on this plate.

Duane and Patterson have found La_2 about .7 per cent. longer than γ_2 and this was confirmed. It appears to be nearly coincident with γ_7 (1.072 Å.). The third absorption limit was too weak to show on this plate. This would indicate that the line γ_2 must belong in L_3. Experimentally the point is still uncertain. A series of photographs at 18, 16, and 15 kv. in platinum showed no noticeable change in intensity ratio between γ_2 and γ_3. On the other hand Dauvillier[4] has reported that γ_2 belongs in L_2 and γ_3 in L_3 in uranium.

STANFORD UNIVERSITY.

RECENT OBSERVATIONS OF ABSORPTION SPECTRA.

BY ARTHUR S. KING.

EXPERIMENTS with the electric furnace in obtaining absorption spectra by the use of a plug at the center of the tube have been directed mainly toward making the method more effective in producing in absorption the more difficult types of lines. With a new furnace, plug temperatures above 3200° C. have been used.

The observations have been largely of the iron spectrum. Iron lines to the red of λ5500 are difficult to reverse, having been previously obtained as absorption lines in the laboratory only in the explosion spectrum. In the emission spectrum of the furnace, they are relatively difficult of production, belonging largely in Class III. This orange and red section of the iron spectrum was obtained in absorption as far as λ6700 by the use of high temperatures, practically all of the furnace lines appearing.

In the ultra-violet, the lines are easily reversed, but the difficulty is to obtain a sufficiently strong continuous ground. This was produced by a plug temperature of 3000° C., the furnace lines being photographed in absorption as far as λ2448.

Between these limits, an extensive study has been made of the iron spectrum

[1] Webster, Proc. Nat. Acad. Sci., 6, 26, 1920.

[2] Hoyt, Proc. Nat. Acad. Sci., 6, 639, 1920.

[3] Loc. cit.

[4] Compt. Rend., 176, 1350, 1921.

in emission and absorption at different temperatures, which will later be reported in detail.

The furnace has also been used to obtain in absorption the subordinate series lines of the alkalis, which had not previously been observed as absorption lines. High temperature, together with the exclusion of oxygen, proved sufficient to bring out in absorption the subordinate series of sodium, potassium, caesium and rubidium. The extreme sharpness and freedom from dissymmetry of these absorption lines have enabled wave-length measurements to be made of greater accuracy than those previously made from arc spectra.

A further use of the absorption furnace was the mounting of a small tube inside a solenoid made to carry heavy currents and giving a strong magnetic field. In one of these solenoids, the furnace could be turned at different angles to the magnetic field. The trials made showed this to be a useful arrangement for the study of absorption lines produced under conditions which approximate in some respects those prevailing in sun-spots.

MOUNT WILSON OBSERVATORY.

PRELIMINARY MEASUREMENTS OF THE CRITICAL POTENTIALS OF THE M LINES IN THE X-RAY SPECTRUM OF LEAD.

BY P. A. ROSS.

THE critical potentials of five lines in the M series of lead have been measured. They are:

Line λ A°	Crit. Pot. in kv.	Edge of Gen. Radiation.
α 5.2751[1]	2.5	4.9 Å
β 5.0648[1]	2.7	4.7
γ 4.6637[1] }	3.1	4.0
δ 4.073[2] }		
ϵ 3.94[3]	4.0	3.1

A water jacketed brass x-ray tube with a Coolidge cathode was kept exhausted by a Langmuir pump. The direct current was supplied by the high tension system of D. L. Webster described elsewhere by him.[4] A stationary gypsum crystal was used with an optical path from target to plate of 24 cm.

This work is still in progress.

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A POSSIBLE ORIGIN OF THE DEFECT OF THE COMBINATION PRINCIPLE IN X-RAYS.

BY ARTHUR H. COMPTON.

THE original Kossel relation, which represents an application of Ritz's combination principle to x-ray spectra, and which follows directly from Bohr's

[1] Stenström. [2] Karcher. [3] Ross.

[4] Proc. Nat. Acad. Sci., vol. 6, p. 269, May, 1920.

theory, states that

$$K_{\alpha_1}+L_{\alpha_1}=\frac{1}{h}(W_{M_1}-W_K)=K_\beta,$$

where K_α, L_α, K_β represent the frequencies of these lines respectively, W_{M_1} is the energy of an electron in the M_1 orbit and W_K its energy in the K orbit. It has been found experimentally, on the other hand, that

$$K_{\alpha_1}+L_{\alpha_1}=\frac{1}{h}(W_{M_1}-W_K)\neq K_\beta,$$

and that the difference

$$\Delta = K_{\alpha_1}+L_{\alpha_1}-K_\beta$$

is of the order of $+\frac{1}{2}$ per cent. of K_β. This difference has constituted a formidable difficulty for the Bohr-Sommerfeld theory of the origin of spectrum lines.

Perhaps the most obvious explanation of this discrepancy, proposed independently by Kossel[1] and Duane,[2] is that the K_β line may not be due to an electron falling from the same M orbit as the L_{α_1} line. According to Rubinowicz's principle of selection, indeed, no electrons should fall from the M_1 orbit to the K ring, but only from the $M_{2,\ 3\ \text{or}\ 4}$ orbits. On this view, therefore, K_β should equal

$$\frac{1}{h}(W_{M_{2,\ 3\ \text{or}\ 4}}-W_K).$$

A critical examination of the wave-lengths by Sommerfeld[3] and particularly by Birge[4] indicates, however, that this explanation probably does not account completely for the observed difference between K_β and $K_{\alpha_1}+L_{\alpha_1}$. In fact the difference Δ should on Kossel's view be approximately proportional to the 4th power of the atomic number, whereas Sommerfeld finds the experimental values of Δ to be nearly a linear function of N.

An alternative, or perhaps supplementary, explanation of this difference Δ is that as the electron passes from the M to the K orbit, traversing the L orbit, it sets the electrons of the L orbit into oscillation, thus being able itself to radiate less energy than (W_K-W_M) when it reaches the K orbit. We know from a study of the tracks of β-rays and cathode rays through air that energy is lost in thus traversing groups of electrons. If the electron which gives rise to the radiation moves gradually from the M to the K orbit, the electrons of the L ring will assume their new positions gradually, and the work done on these electrons will be the same as that done by successive transfers from M to L, producing the L_α line, and from L to K, producing the K_α line. In this case the combination principle should therefore hold. If, however, the radiating electron were transferred instantaneously from the M to the K

[1] Kossel, Zeitschr. f. Phys., 1, 126, 1920.

[2] Duane and Stenström, Nat. Ac. Sci. Proc., 6, 484, 1920.

[3] Sommerfeld, Zeitschr. f. Phys., 1, 142, 1920.

[4] Birge, PHYS. REV., 16, 371, 1920.

orbit, the electrons of the L ring would be set into oscillation with an energy equal to their difference in energy for p and for $p-1$ electrons in the inner ring. Such energy of oscillation must be taken from the falling electron, and can be shown to represent a loss in frequency of this electron's radiation by approximately

$$\Delta = \frac{1}{h}\Delta W = \frac{2qR}{2^2}(N - p - \varphi_q), \tag{1}$$

where p and q are the numbers of electrons in the K and L rings respectively, R is the Rydberg constant, N is the atomic number, and φ_q is Moseley's correction for the repulsion between the electrons in the L ring. The energy spent by the radiating electron in setting up oscillations in the ring of electrons through which it passes will therefore lie between zero and the value represented by expression (1). The fact that this view makes Δ a linear function of N is in accord with Sommerfeld's interpretation of the experiments, and the numerical values also are of the right order.

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